Phase Field Modelling

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0.1 Solution Models

In this section, we will discuss a specific model used to comprehend the thermodynamics of alloy systems, known as the regular solution model. It is common knowledge that metals like nickel, copper, and silver crystallize in cubic structures, specifically the face-centered cubic system, while zinc crystallizes in a hexagonal structure. When two different crystals, such as nickel and copper, are combined, they form a solid solution.

Over a century ago, it became evident that complex phenomena arise when different types of atoms are mixed. For instance, nickel and copper form an isomorphous system, being completely immiscible in both solid and liquid states. Conversely, copper and silver form a eutectic system. Nickel and aluminum exhibit various altered structures, whereas aluminum and zinc phase separate.

The regular solution model, which we will delve into, aims to elucidate the behavior of different atoms when combined. It is based on Gibbs free energy. At constant temperature and pressure, equilibrium can be understood as minimizing Gibbs free energy, represented as:

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

In condensed systems (solids and liquids), it is a reasonable approximation to equate enthalpy with internal energy, neglecting the pV term:

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

Consider a system composed of two types of atoms, A and B. One of the simplest models is to examine what happens when A and B are combined in a solid binary alloy at normal atmospheric pressure. The most basic thermodynamic model for this scenario is the Ideal Solution. Before discussing it, let's define the free energy of mixing. Assume there are some A-type (black) and B-type (red) atoms, each associated with a certain free energy. Upon combining them, the resulting configuration possesses its own free energy. The difference between this configuration's free energy and the free energy of the separate initial conditions is termed the free energy of mixing:

$$\Delta G^{Mix} = \Delta U^{Mix} - T\Delta S^{Mix} \tag{3}$$
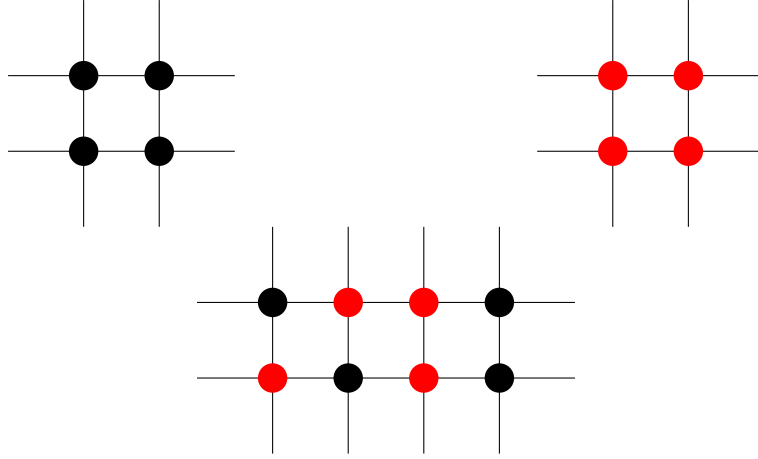
In the realm of atomic-level mixing, various mechanisms can drive the process, each aiming to maximize the reduction of ΔG^{Mix} making it as negative and sizable in magnitude as possible. Among these mechanisms, the preferred one is the one that achieves the most significant reduction.

For the ideal solution, it is postulated that ΔU^{Mix} is zero. Another assumption prevalent in many alloy models is that entropy's only significant contribution arises from configurational entropy:

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

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

$$S = k\,ln(\omega) \tag{4}$$

Where ω is the number of possible configurations (microstates) for distributing N_A A atoms and N_B B atoms on a lattice of size $N = N_A + N_B$. If the distinction between the A and B atoms cannot be made (all N_A are equal and all N_B are identical), then the following expression is applicable:

$$\omega = \frac{N!}{N_A!\,N_B!} \tag{5}$$

Initially, when there are only A and B atoms, the configuration entropy is zero as $\omega = 1$, implying zero entropy.

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

For large values of N, the Sterling approximation can be utilized:

$$ln(N!) = Nln(N) - N \tag{7}$$

$$\Delta S^{Mix,Config.} = k\left[ln(N!) - ln(N_A!) - ln(N_B!)\right]$$
$$= k\left[Nln(N) - N - N_Aln(N_A) + N_A - N_Bln(N_B) + N_B\right]$$
$$= k\left[(N_A + N_B)ln(N) - N_Aln(N_A) - N_Bln(N_B)\right]$$
$$= -k\left[-N_Aln(N) - N_Bln(N) + N_Aln(N_A) + N_Bln(N_B)\right]$$
$$= -k\left[N_Aln\left(\frac{N_A}{N}\right) + N_Bln\left(\frac{N_B}{N}\right)\right] \tag{8}$$
$$= -k\left[N_Aln(X_A) + N_Bln(X_B)\right]$$
$$= -kN\left[\frac{N_A}{N}ln(X_A) + \frac{N_B}{N}ln(X_B)\right]$$
$$= -kN\left[X_Aln(X_A) + X_Bln(X_B)\right]$$

Where X_A and X_B represent the atomic fractions of A and B respectively

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

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

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

Both T and R are positive quantities, and since the logarithm of a fraction (a number less than 1) is negative, the entirety of ΔG^{Mix} is less than 0.

The term "ideal solution" is aptly named because it uniformly mixes A and B atoms, achieved through perfect random arrangement on the lattice. Furthermore, it's termed "ideal" because the system cannot distinguish between A and B atoms, resulting in an internal energy of mixing of 0.

The subsequent model, slightly more intricate than the ideal solution, is the regular solution model. In this model, ΔS^{Mix} is still solely dictated by configurational entropy. Additionally, the assumption of random distribution of A and B atoms remains valid, and the same expression derived for the ideal solution holds. Moreover, let's assume that ΔH^{Mix}, previously assumed to be zero in the ideal solution case, is now a small nonzero value, $\Delta H^{Mix} << 1$. ΔH^{Mix} is influenced by differences in bond energies (AA, BB, AB). At higher temperatures, entropy dominates, whereas at very low temperatures, enthalpy becomes dominant.

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

Where Ω is known as the regular solution parameter

$$\Omega = N_{Avog.}\zeta\epsilon \tag{12}$$

Where ζ is the number of nearest neighbours in the crystal structure

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

this one represents the difference in the bond energies. Let consider two AA and BB bounds, break them and make AB bounds and ϵ 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

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

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

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
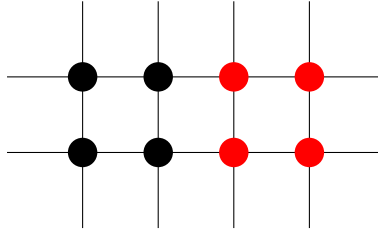
On the other hand, suppose making AA and BB bonds is very expensive in terms of energy and if it brakes them making AB bonds is cheaper, then the configuration is assisted to have just AB bonds like in the picture and is called ordered crystal structure
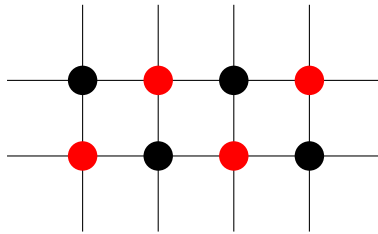
At any temperature above the absolute, the entropy is always trying to make the system goes to a more random configuration, and It prefers neither of the previous two because them are too ordered from entropy point of view.
The models that will be talk about in this course, are basically models meant 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:

$$E = p_{AB}E_{AB} + p_{AA}E_{AA} + p_{BB}E_{BB} \tag{16}$$

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:

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

the same can be done for B

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

The total energy becomes:

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

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

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

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

the same can be done for AA and BB:

$$p_{AA} = X_A^2 \qquad p_{BB} = X_B^2 \tag{22}$$

Finally, the following is obtained:

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

0.2   G vs X Diagrams

The plot of the ΔH^{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, ΔG^{Mix} can be seen that the entropy term is dominant at the corners of the diagram but then the ΔH^{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 $\Omega > 0$.
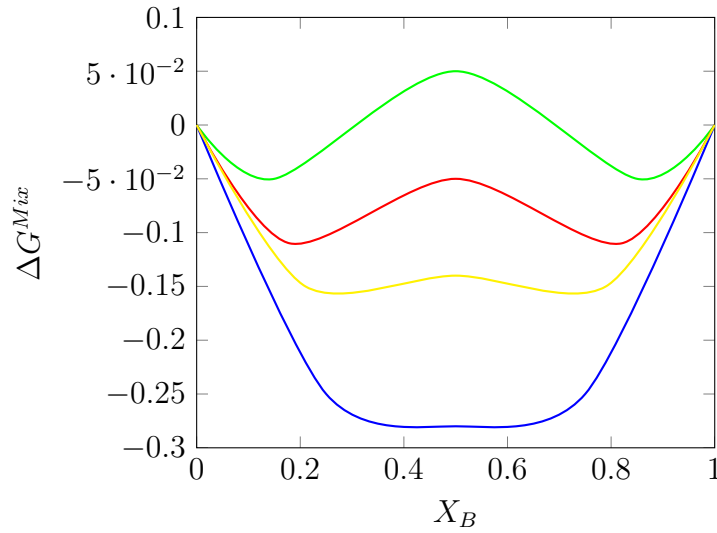

Figure 1: Gibbs free energy of binary mixtures as a function of the composition at constant pressure and temperature. The green curve is at low temperature, instead red, yellow and blue are curves in which the temperature is increasing

0.3 Phase Diagrams

If ones want to know the free energy of the mix itself G, It is calculated in this way:

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

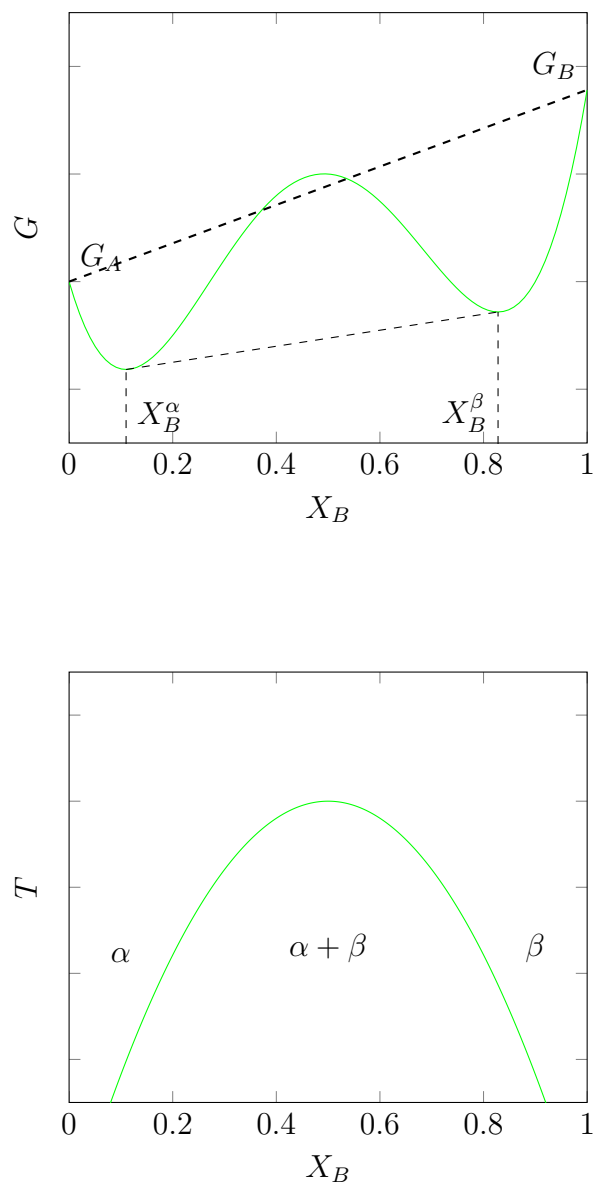The first two terms added are just a straight line and the plot becomes:

Figure 2: The green curve is for law 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

7

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^α and X_B^β. 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:

$$dG' = \mu_A dn_A \tag{25}$$

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

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

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:

$$dG' = \mu_A dn_A + \mu_B dn_B \tag{27}$$

Now dividing everything by $n_A + n_B$

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

$$dG = \mu_A dX_A + \mu_B dX_B \tag{29}$$

$$\frac{dG}{dX_B} = \mu_A \frac{dX_A}{dX_B} + \mu_B = -\mu_A + \mu_B \tag{30}$$

$$G = \mu_A X_A + \mu_B X_B \tag{31}$$

From here is possible to find:

$$\mu_B = \frac{G - \mu_A X_A}{X_B} \tag{32}$$

and substituting inside (30) is possible to find:

$$\mu_A = G - X_B \frac{dG}{dX_B} \tag{33}$$

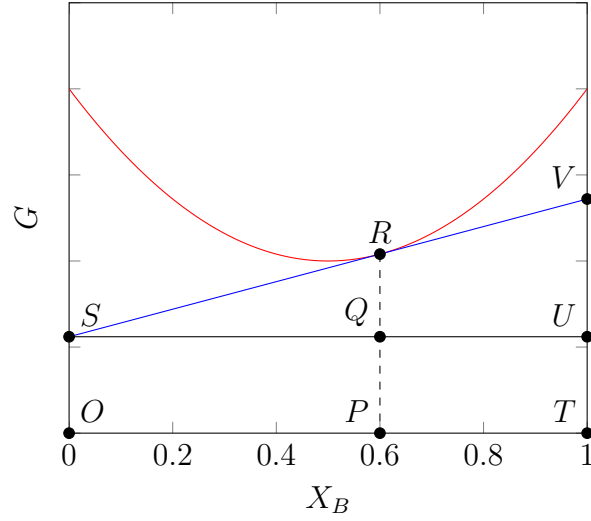Let consider a free energy vs composition diagram as below with the curve in red

Figure 3

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

$$\mu_A = PR - X_B \frac{RQ}{SQ} = PR - X_B \frac{RQ}{X_B} = PR - RQ = PQ = OS \tag{34}$$

Geometrically, μ_A is the point in which the common tangent intersect the pure A axis. From (30) It is possible to calculate μ_B:

$$\mu_B = OS + \frac{UV}{US} = OS + \frac{UV}{1} = OS + UV = TV \tag{35}$$

Geometrically, μ_B is the point in which the common tangent intersect the pure B axis.

9

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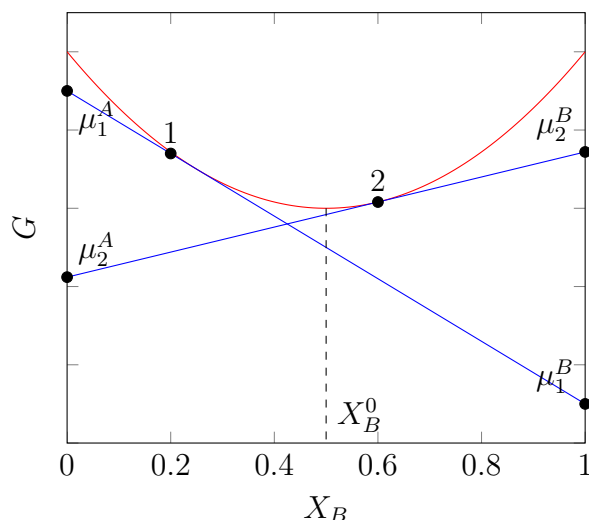
As can be seen, the chemical potential for A in 1 is higher than in 2 and the chemical potential for B in 2 is higher than in 1.

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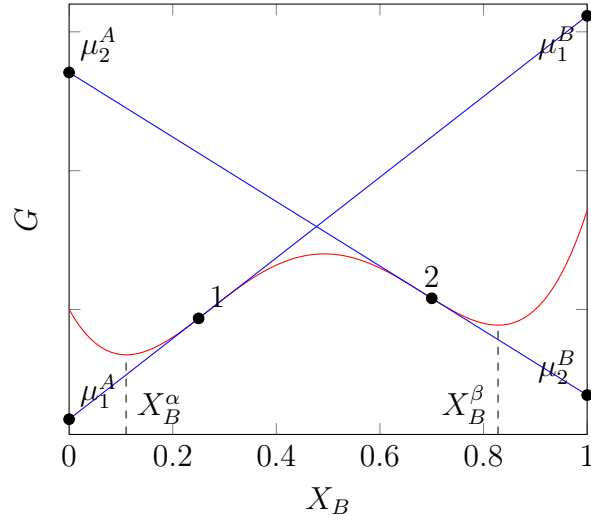
The chemical potential for B in 2 is lower than the chemical potential for B in 1, then the B atoms are going to go from 1 to 2. Similarly, because the chemical potential for A in 1 is lower than the chemical potential for A in 2, the A atoms are going to go from 2 to 1. At the end, there will get a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

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:

$$\mathbf{J} = -D\nabla C \tag{36}$$

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

$$\frac{\partial C}{\partial t} = -\nabla \cdot \mathbf{J} \tag{37}$$

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

$$\frac{\partial C}{\partial t} = D\nabla^2 C \tag{38}$$

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 fluxed allowed. The Fick's first law is modified to this one:

$$\mathbf{J} = -M\nabla\mu \tag{39}$$

Where M is called mobility that is always positive.

0.7 Spinoidal decomposition

The following plot is valid if the α and β 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 separated the matastable region from the unstable region. Points inside the spinoidal are unstable points instead points outside but, at the same time inside the miscibility gap, are metastable points.
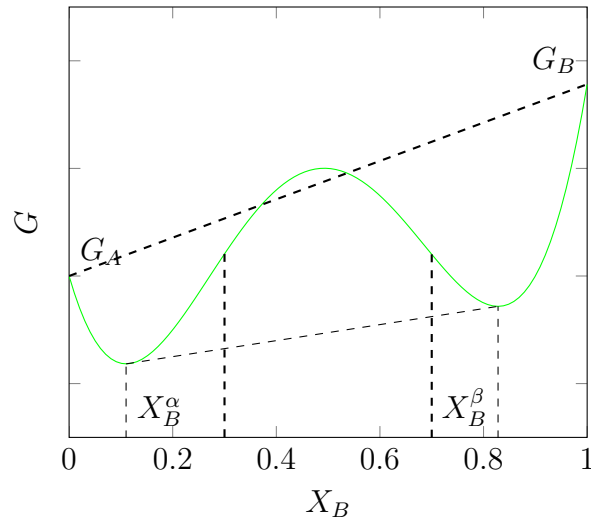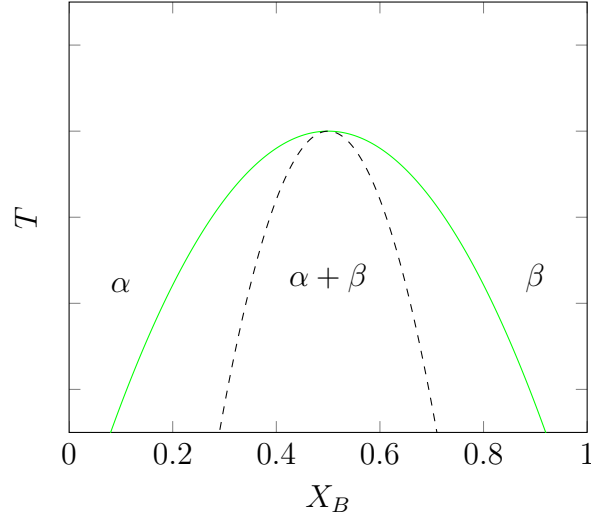

Figure 4

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 in 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:

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

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:

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

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

13

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

$$\Delta Y = \Delta Y^a + \Delta Y^b = X_B' \left[\bar{Y}_2(X_B') - \bar{Y}_2(X_B^0) \right] + (1 - X_B') \left[\bar{Y}_1(X_B') - \bar{Y}_1(X_B^0) \right]$$
$$= X_B' \bar{Y}_2(X_B') + (1 - X_B')\bar{Y}_1(X_B') - X_B^0 \bar{Y}_2(X_B^0) - (1 - X_B^0)\bar{Y}_1(X_B^0) + \qquad (42)$$
$$+ (X_B^0 - X_B') \left[\bar{Y}_2(X_B^0) - \bar{Y}_1(X_B') \right]$$

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

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':

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

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

Comparing (45) and (43) yields:

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

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

For example, considering the free energy:

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

The sign of the change in free energy is given by the sign of $G''(c_0)$.
If $G''(c_0) < \Rightarrow \Delta G < 0$ 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.
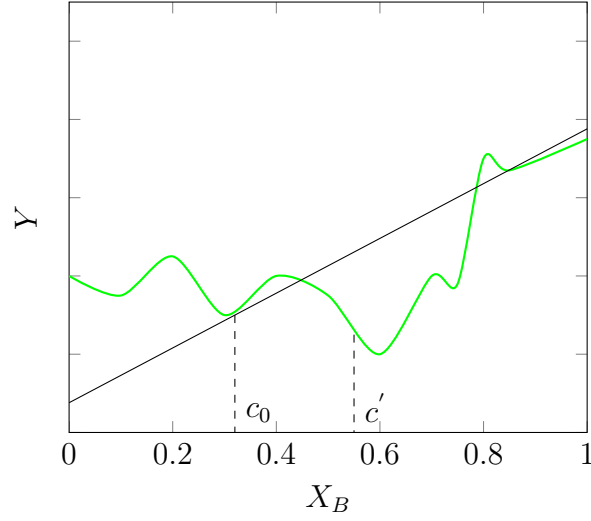
The vertical distance of $Y(c')$ from the straight line is ΔY. For all the points below the tangent to $Y(c_0)$ (straight line), $\Delta Y < 0$.

0.8   Solution of classical diffusion equation

We want to solve the following differential equation:

$$\frac{\partial c}{\partial t} = D\nabla^2 c \tag{49}$$

In 1-D becomes:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \tag{50}$$

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

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

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

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

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

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

The solution can be achieved by separating the variables:

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

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

$$A = A_0 exp(-D\beta^2 t) \tag{56}$$

0.9   Diffusivity and Mobility

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

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

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 μ_1 is the chemical potential per atom.
The same can be done for the component 2:

$$J_2 = -N_V c\, v_2 \frac{\partial \mu_2}{\partial x} \tag{58}$$

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:

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

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

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

Where the mobility is defines as:

$$M = c(1 - c) \left[(1 - c)v_2 + cv_1 \right] \tag{61}$$

We know that:

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

and the flux becomes:

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

We know from mass conservation:

$$\frac{\partial c}{\partial t} = -\frac{1}{N_V} \frac{\partial J}{\partial x} \tag{64}$$

and placing (63) into (64) yields:

$$\frac{\partial c}{\partial t} = \frac{1}{N_V} \frac{\partial}{\partial x} \left(M G'' \frac{\partial c}{\partial x} \right) \tag{65}$$

Assuming that M and G'' constants, then:

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

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

$$D = \frac{M}{N_V} G'' \tag{67}$$

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

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

$$A = A_0 exp\left(R(\beta)t\right) \tag{69}$$

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 β, 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 β.

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 β value is. If β becomes larger and larger or the same if λ becomes smaller and smaller, than growth is really fast because it's exponentially growing. The λ 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 $\lambda = 100$.

This equation is known as Cahn-Hilliard eq. :

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

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:

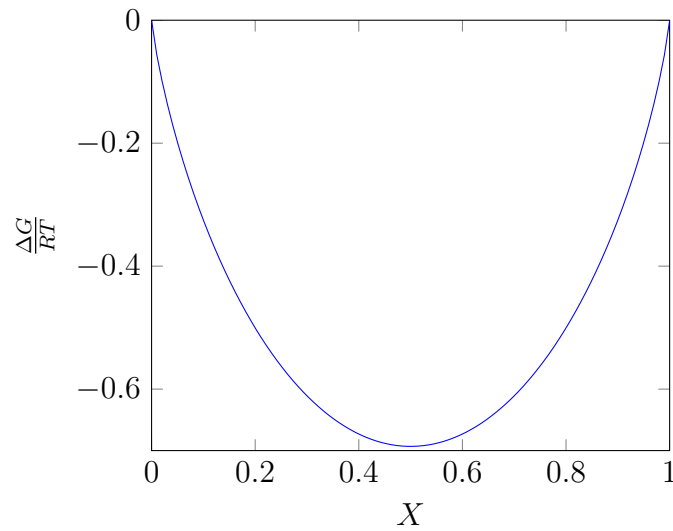$$\frac{\Delta G}{RT} = \Big[Xln(X) + (1-X)ln(1-X) \Big] \tag{71}$$

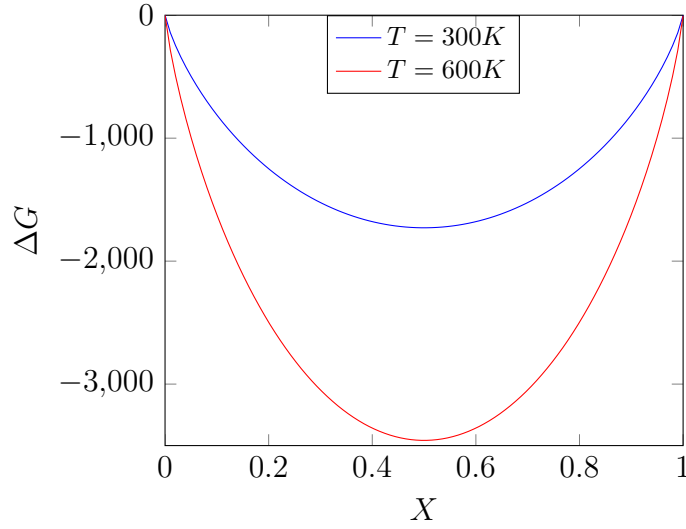Figure 6: Plot of the dimensionless free energy vs composition

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:

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

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
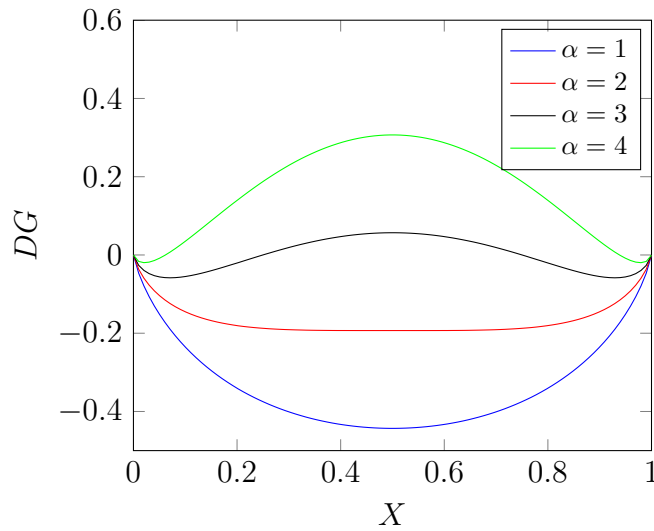
Figure 8: Plot of the dimensionless free energy vs composition at different α

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')
```

0.15 Plotting spinoidal line on MATLAB

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

$$DG'' = -2\alpha + \frac{1}{X} + \frac{1}{1-X} \tag{74}$$

```
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')
```

0.16 Non-dimensionalization of diffusion equation

The Fick's seconds law is:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \tag{75}$$

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.
τ and L_0 are the characteristic time and length choose. The equation becomes:

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

$$\frac{\partial c}{\partial t^*} = D^*\frac{\partial^2 c}{\partial x^{*2}} \tag{77}$$

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):

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \tag{78}$$

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:

$$c(x, t) = F(x)G(t) \tag{79}$$

and substituting inside the partial differential equation, yields:

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

$$F\frac{\partial G}{\partial t} = D\,G\frac{\partial^2 F}{\partial x^2} \tag{81}$$

$$\frac{\dot{G}}{D\,G} = \frac{1}{F}F'' \tag{82}$$

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:

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

$$\frac{\dot{G}}{D\,G} = -p^2 \Rightarrow \dot{G} + p^2 D\,G = 0 \tag{84}$$

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

$$F(x) = A cos(p\,x) + B sin(p\,x) \tag{85}$$

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 $F(L) = 0$.

$$F(0) = A = 0 \tag{86}$$

$$F(L) = B sin(p\,L) = 0 \tag{87}$$

but we do not want the trivial solution $B = 0$ and so $sin(p\,L) = 0 \Rightarrow p\,L = n\pi \Rightarrow p = \frac{n\pi}{L}$ with $n = 1, 2, ...$
The solution for the position dependent part is:

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

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

$$\dot{G} + \frac{n^2\pi^2 x^2}{L^2}D\,G = 0 \tag{89}$$

24

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

$$\dot{G} + \lambda_n^2 \, G = 0 \tag{90}$$

where the solution is:

$$G_n(t) = k_n exp(-\lambda_n^2 \, t) \quad n = 1, 2, ... \tag{91}$$

The total solution is:

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

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

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

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

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

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

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:

$$\eta = \frac{c - c_i}{c_0 - c_i} \tag{97}$$

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:

$$\frac{\partial \eta}{\partial \tau} = \frac{D \, t_0}{L^2} \frac{\partial^2 \eta}{\partial \zeta^2} \tag{98}$$

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:

$$\frac{\partial \eta}{\partial \tau} = \frac{\partial^2 \eta}{\partial \zeta^2} \tag{99}$$

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:

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

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 $\frac{d\eta}{dy} = p$.

$$\frac{\partial \eta}{\partial \tau} = \frac{\partial \eta}{\partial y} \frac{\partial y}{\partial \tau} \tag{101}$$

$$\frac{\partial y}{\partial \tau} = -\frac{1}{2} \frac{\zeta}{\tau \sqrt{\tau}} = -\frac{y}{2\tau} \tag{102}$$

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

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

The equation becomes the following ordinary differential equation:

$$-\frac{d\eta}{dy} \frac{y}{2\tau} = \frac{1}{\tau} \frac{d^2\eta}{dy^2} \Rightarrow \frac{dp}{dy} = -\frac{y\,p}{2} \tag{105}$$

Integrating this equation, the solution is:

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

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

0.19 Finite difference method

Suppose to have the domain and discretize it. Each discrete part is of length Δx and so the number of pieces is $n = \frac{L}{\Delta x}$. Also the time should be discretized by Δt.
The first derivative in time at the i-th position, is approximated as:

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

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

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

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

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

The diffusion equation becomes:

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

At any position i, the composition at the future time Δt is:

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

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:

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

and we end by:

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

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

$$\begin{bmatrix} 1+2\alpha & -\alpha & 0 & 0 & 0 & \dots & 0 \\ -\alpha & 1+2\alpha & -\alpha & 0 & 0 & \dots & 0 \\ 0 & -\alpha & 1+2\alpha & -\alpha & 0 & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & \dots & -\alpha & 1+2\alpha \end{bmatrix} \begin{bmatrix} c_1^{t+\Delta t} \\ c_2^{t+\Delta t} \\ c3^{t+\Delta t} \\ \vdots \\ c_n^{t+\Delta t} \end{bmatrix} = \begin{bmatrix} c_1^t \\ c_2^t \\ c_3^t \\ \vdots \\ c_n^t \end{bmatrix}$$

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 $\left(\frac{\partial c}{\partial x}\right)_{x=L} = 0$. The initial condition is $c(x,0) = 0$ for $x > 0$.
We have that from the first BC:

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

and for the second BC:

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

from which:

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

```
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 colums inizialized 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
```

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 raw 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 -2α.

```
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 colums inizialized 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
```
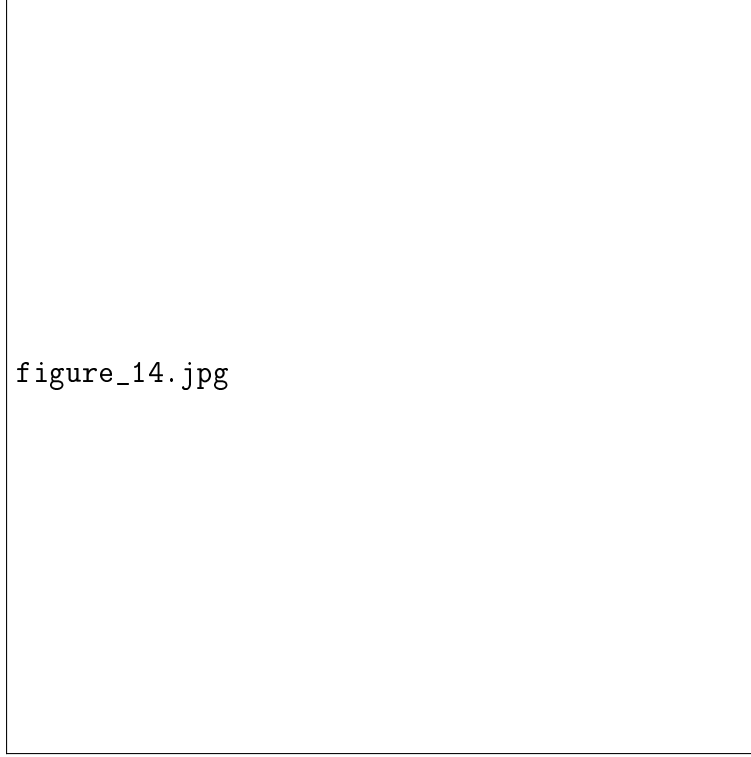
figure_14.jpg

Figure 9

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 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:

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

Applying the Fourier transform to the diffusion equation yields:

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

Putting the derivative inside the integral we obtain the ODE:

$$\frac{d\widetilde{c}}{dt} = -Dk^2\widetilde{c} \tag{120}$$

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:

$$\frac{\widetilde{c}^{t+\Delta t} - \widetilde{c}^{t}}{\Delta t} = -Dk^2\widetilde{c}^{t+\Delta t} \tag{121}$$

$$\widetilde{c}^{t+\Delta t} = \frac{\widetilde{c}^{t}}{1 + D\,k^2\Delta t} \tag{122}$$

This method is very stable because there are not restrictions on the size of Δt. 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
```

0.22   Scalar, vectors and tensors

The Fick's first law says that:

$$\mathbf{J} = -D\nabla c \tag{123}$$

where both $\mathbf{J}$ and ∇c are vectors. The vectors are quantities with a magnitude and a direction. Scalars are quantities with only magnitude like c. The diffusivity D is a second rank tensor.

The vectors can be seen as first rank tensors and scalar as zero rank tensors.

Defining a reference frame, the vector can be represented as:

$$\bar{J} = (J_1, J_2, J_3) = J_i \quad i = 1, 2, 3 \tag{124}$$

Sometimes is represented as matrix notation like this:

$$\bar{J} = \begin{pmatrix} J_1 \\ J_2 \\ J_3 \end{pmatrix} \tag{125}$$

Scalars are quantities with no indices (that why zero rank tensors). Vectors are quantities with one index (that why first rank tensors). Tensors are quantities with two indices.

$$\nabla c = \begin{pmatrix} \frac{\partial c}{x_1} \\ \frac{\partial c}{x_2} \\ \frac{\partial c}{x_3} \end{pmatrix} = \nabla_i c \tag{126}$$

The most generic Fick's first law referred to a fixed reference frame is:

$$\begin{pmatrix} J_1 \\ J_2 \\ J_3 \end{pmatrix} = - \begin{pmatrix} D_{11} & D_{12} & D_{13} \\ D_{21} & D_{22} & D_{23} \\ D_{31} & D_{32} & D_{33} \end{pmatrix} \begin{pmatrix} \frac{\partial c}{x_1} \\ \frac{\partial c}{x_2} \\ \frac{\partial c}{x_3} \end{pmatrix} \tag{127}$$

where D is a second rank tensor. The same expression can be written in a compact way using the Einstein's summation convention:

$$J_i = D_{ij}\nabla_j c \tag{128}$$

In a tensor notation, where is not referred to any reference frame, the equation is written as:

$$\bar{J} = \bar{\bar{D}}\nabla c \tag{129}$$

33

The vectors have a life of their own. They are physical quantities that does not depend on which frame of reference we choose to describe it.

Let's choose a reference frame (x, y, z) to describe a certain vector. Let's take another reference frame centered in the first one but rotated respect to it (x', y', z') as can be seen in the picture. The relationship between the two reference is given by the transformation matrix
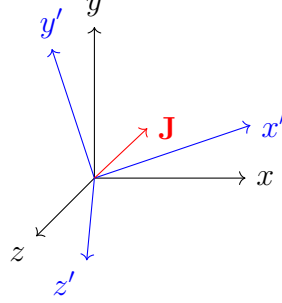
$$x'_i = a_{ij}x_j \quad \Rightarrow \quad x_i = a_{ji}x'_j \tag{130}$$

$$\begin{pmatrix} x'_1 \\ x'_2 \\ x'_3 \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} \tag{131}$$

where a_{ij} are the direction cosines for x'_i with x_j. We says that j is the dummy index and it should be repeated two times. The true vector is a quantities in which changes its coordinates when a reference frame is changed and the relationship between the two coordinates is governed by (130).

Transformation matrices relate vector components in different frames, enabling a consistent definition. This concept extends to tensors, including diffusivity tensors, which represent properties and have an independent existence from matrix representations.

Transformation matrices differ from property tensors, with the former acting as bridges between frames and the latter having an existence independent of frames.

We define what is a second rank tensor in terms of the transformation matrix. We know that in the regular frame of reference, the flux is expressed as (128) and inserting it inside (130):

$$J'_i = -a_{ij}D_{jk}\nabla_k c \tag{132}$$

We can also express the gradient of the concentration in the new reference frame by:

$$\nabla_k c = a_{lk}(\nabla_l c)' \tag{133}$$

and replacing it inside (132) yields:

$$J_i' = -a_{ij}D_{jk}a_{lk}(\nabla_l c)' \tag{134}$$

From this equation is possible to understand that the diffusivity tensor can be written in the new reference frame suing this relation:

$$D_{il}' = a_{ij}D_{jk}a_{lk} \tag{135}$$

where in this case k and j are the dummy indices.
The equation becomes:

$$J_i' = -D_{il}'(\nabla_l c)' \tag{136}$$

There is a definition of what is a symmetric tensor and a skew symmetric (or anti-symmetric) tensor. If $D_{ij} = D_{ji}$, then $\bar{\bar{D}}$ is a symmetric tensor, instead if $D_{ij} = -D_{ji}$ then $\bar{\bar{D}}$ is a skew symmetric tensor, where all the diagonal terms are 0.

The Neumann's principle, it says that the symmetry elements of any physical property of a crystal must include the symmetry elements of the point group of the crystal.

If we do an operation on an entity and if we cannot figure out after the operation is complete that we have carried out such an operation, then that entity is said to have this symmetry. This symmetry operation that we are talking about could be a mathematical operation or the entity could be a geometric thing which is what it is in the case of crystals and the operation could be geometric operation, it could be a rotation, it would be a reflection, it could be a combination of the two.
What Neumann's principle says is that, if we have a square it should have at least the symmetry of square, it can have higher symmetry like that of a circle, but it cannot have lower symmetry like that of a tetragonal for example or of a rectangle for example.

0.23   Group theory

Let us consider a set which consists of four elements namely $(+1, -1, +i, -i)$. We can form a multiplication table consisting of these four numbers:

$\cdot$	1	-1	i	$-i$
1	1	-1	i	$-i$
-1	-1	1	$-i$	i
i	i	$-i$	-1	1
$-i$	$-i$	i	1	-1

there are certain properties which are satisfied in this kind of multiplication table:

1) Closure; the multiplication table consists of only of these four numbers and under the multiplication operation we get the same four numbers in different combinations

2)Associativity; the order in which we multiply is not important

3)Existence of unit element; for every element A, there is one element I which, if we multiply it by A, we get the same element $A\,I = I\,A = A$

4)Existence of inverse element A^{-1} in which $A^{-1}A = A\,A^{-1} = I$

If we have a set of elements and if we can define an operation on this set of elements, under the action of this operation if the elements satisfies these four properties, then that is a known as a group.

Let us consider another set $(0, \frac{\pi}{2}, \pi, \frac{3\pi}{2})$. We can form an addition table consisting of these four numbers:

| $+$	0	$\frac{\pi}{2}$	π	$\frac{3\pi}{2}$
0	0	$\frac{\pi}{2}$	π	$\frac{3\pi}{2}$
$\frac{\pi}{2}$	$\frac{\pi}{2}$	π	$\frac{3\pi}{2}$	0
π	π	$\frac{3\pi}{2}$	0	$\frac{\pi}{2}$
$\frac{3\pi}{2}$	$\frac{3\pi}{2}$	0	$\frac{\pi}{2}$	π

It can be seen that this forms a group under the addition operation.

0.24 Crystal:symmetric elements

Let us consider an equilateral triangle. We define a symmetry operation as an operation that leaves this triangle unchanged. For example, if we take its center of gravity and perform a 120-degree rotation about an axis passing through the center, the triangle will appear identical
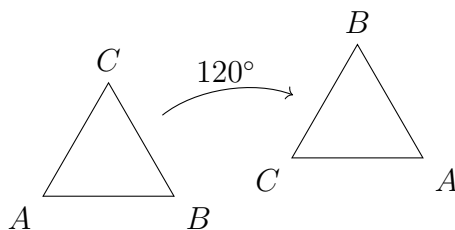
There are 3 symmetric rotation operations which are $A = 120°, B = 240°, I = 0°$. There are also other 3 operations which are the reflection operation about the three lines do determine the center of the triangle that we call F, G, H.
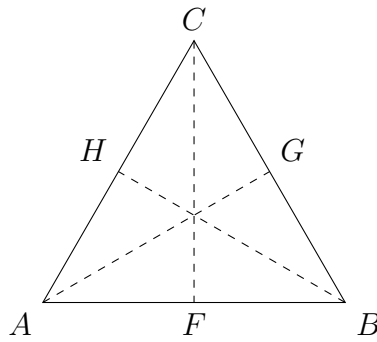
The 6 operations form a group and are symmetric operations under the addition and multi-plication and this is known as point group symmetry.

There is another way to represent the same group, in which the elements of the group can be represented by a matrices

$$I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad A = \frac{1}{2}\begin{pmatrix} -1 & -\sqrt{3} \\ \sqrt{3} & -1 \end{pmatrix} \quad B = \frac{1}{2}\begin{pmatrix} -1 & \sqrt{3} \\ -\sqrt{3} & -1 \end{pmatrix}$$

$$F = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \quad G = \frac{1}{2}\begin{pmatrix} 1 & -\sqrt{3} \\ -\sqrt{3} & -1 \end{pmatrix} \quad H = \frac{1}{2}\begin{pmatrix} 1 & \sqrt{3} \\ -\sqrt{3} & -1 \end{pmatrix}$$

A lattice is basically points in space which are periodic. If with every lattice we associate certain atoms or molecules (known as motif), the lattice plus the motif makes the crystal structure.

This crystal structure can be explained of what is known as unit cell. There are many different unit cells, for example the simple cubic unite cell
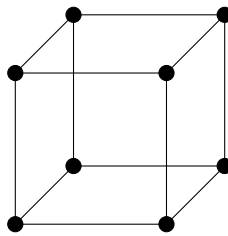

There are several symmetric elements. One is known as center of symmetry (or Inversion). Suppose to have the (x, y, z) centered at the center of the unit cell and we invert the axis into $(-x, -y, -z)$.

Another symmetry operation is known as mirror plane. Also the n-fold rotation, which can be $1, 2, 3, 4$ or 6-fold, that means we rotate of $\frac{2\pi}{n}$, is a symmetric group.

This operations combined together form a group called point group symmetry.

0.25   Variational calculus

Let us consider some function $f(x)$ as in the picture
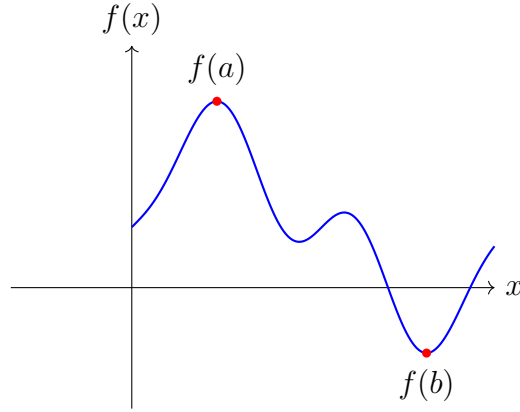
if we want to know where the maxima or minima of $f(x)$ are, the sufficienty and necessary conditioned can be obtained by looking the Taylor series expansion.

We are looking at a point a which is an extreme point as is shown in the picture, and we do a Taylor series expansion about $f(a)$

$$f(x) = f(a) + (x-a)f^{'}(x)|_{x=a} + \frac{(x-a)^2}{2!}f^{''}(x)|_{x=a} + ... \tag{137}$$

we know that if we are at a maxima point $f(x) - f(a) < 0$. But we know that

$$f(x) - f(a) = (x-a)f^{'}(x)|_{x=a} + \frac{(x-a)^2}{2!}f^{''}(x)|_{x=a} + ... \tag{138}$$

and this is only valid if $f^{'}(x)|_{x=a} = 0$ and $f^{''}(x)|_{x=a} < 0$.

Suppose now to chose another point b which is the minimum. Then it is easy to see graphically that $f(x) - f(b) > 0$ and this is only valid if $f^{'}(x)|_{x=b} = 0$ and $f^{''}(x)|_{x=b} > 0$ This is valid for finding the global minima and global maxima.

A functional instead is a function of a function. The easieat way to understand the functional is to look at the quantity called action functional, which is defined in classical mechanics:

$$\mathcal{L} = \int_{t_1}^{t_2} \{T - V\}\, dt = \int_{t_1}^{t_2} \left\{\frac{1}{2}m\,\dot{x}^2(t) - V(x(t))\right\} dt = \int_{t_1}^{t_2} F(t, x(t), \dot{x}(t)) dt \tag{139}$$

where T is the kinetic energy and V is the potential energy and t is the independent variable. This was an example of functional.

There are different functionals. The brachistochrone problem is a shortest time problem defines as follows: Considering two points in the plane at different high y_1 ed y_2 with $y_1 > y_2$ and we connect them with a chute. On the top of it, we have a particle with a certain velocity v_1 in a gravitational field that must reach the second point on the bottom. We want to know the chute shape that guarantied the shortest time to reach the bottom point.

$$v = \frac{ds}{dt} \quad \Rightarrow \quad dt = \frac{ds}{v} \tag{140}$$

The total travel time functional is:

$$I = \int_1^2 \frac{ds}{v} = \int_1^2 \frac{\sqrt{dx^2 + dy^2}}{v} = \int_{x_1}^{x_2} \frac{\sqrt{1 + y'^2(x)}}{v} dx \tag{141}$$

The velocity can be found doing the conservation of mechanical energy from the top point at $y = y_1$ and a generic high y:

$$\frac{1}{2}mv_1^2 + mgy_1 = \frac{1}{2}mv^2 + mgy \implies v = \sqrt{v_1^2 - 2g(y_1 - y(x))} \tag{142}$$

and inserting inside (141):

$$I(y) = \int_{x_1}^{x_2} \frac{\sqrt{1 + y'^2(x)}}{\sqrt{v_1^2 - 2g(y_1 - y(x))}} dx \tag{143}$$

0.26 Optimization of functionals

Consider the following generic functional that we want optimize:

$$I = \int_{x_1}^{x_2} F(x, y(x), y'(x)) dx \tag{144}$$

We assume that there is a function $y(x)$ that extremize the functional I. We are going to define an admissible set of functions:

$$\tilde{y}(x) = y(x) + \epsilon \eta(x) \tag{145}$$

where $\eta(x_1) = \eta(x_2) = 0$ and ϵ is a small scalar parameter for the variation of $y(x)$. Let us consider the varied functional:

$$\tilde{I} = \int_{x_1}^{x_2} F(x, \tilde{y}(x), \tilde{y}'(x)) dx \tag{146}$$

$$\tilde{I} = \int_{x_1}^{x_2} F(x, y(x) + \epsilon \eta(x), y'(x) + \epsilon \eta'(x)) dx \tag{147}$$

Since that depends on only ϵ, we can do a Taylor expansion:

$$\tilde{I} = (\tilde{I})_{\epsilon=0} + \left(\frac{d\tilde{I}}{d\epsilon}\right)_{\epsilon=0} \epsilon + \left(\frac{d^2\tilde{I}}{d\epsilon^2}\right)_{\epsilon=0} \frac{\epsilon^2}{2!} + ... \tag{148}$$

we know that $(\tilde{I})_{\epsilon=0} = I$ and the varietional of I is defines as:

$$\delta I = \tilde{I} - I = \left(\frac{d\tilde{I}}{d\epsilon}\right)_{\epsilon=0} \epsilon + \left(\frac{d^2\tilde{I}}{d\epsilon^2}\right)_{\epsilon=0} \frac{\epsilon^2}{2!} + ... \tag{149}$$

The necessary condition for an extrimum to be achived, is that $\left(\frac{d\tilde{I}}{d\epsilon}\right)_{\epsilon=0} = 0$. So we can say that:

$$\begin{aligned}\left(\frac{d\tilde{I}}{d\epsilon}\right)_{\epsilon=0} &= \left[\int_{x_1}^{x_2}\left[\frac{\partial F}{\partial\tilde{y}}\frac{d\tilde{y}}{d\epsilon}+\frac{\partial F}{\partial\tilde{y}'}\frac{d\tilde{y}'}{d\epsilon}\right]dx\right]_{\epsilon=0}\\ &= \int_{x_1}^{x_2}\left[\frac{\partial F}{\partial y}\eta+\frac{\partial F}{\partial y'}\eta'\right]dx = 0\end{aligned} \tag{150}$$

Now applying the integration by parts to the second term of the integral and considering the assumption of the function $\eta(x)$ at the extremes, yields:

$$\left(\frac{d\tilde{I}}{d\epsilon}\right)_{\epsilon=0} = \int_{x_1}^{x_2}\left[\frac{\partial F}{\partial y}-\frac{d}{dx}\left(\frac{\partial F}{\partial y'}\right)\right]\eta dx = 0 \tag{151}$$

where over the entire domain shoul be respected that:

$$\frac{\partial F}{\partial y}-\frac{d}{dx}\left(\frac{\partial F}{\partial y'}\right) = 0 \tag{152}$$

This is known as the Euler-Lagrange equation, which is for the first variation, and it is the necessary condition for the functional to have an extreme.
The minimization of the action functional, which is the following:

$$\mathcal{L} = \int_{t_1}^{t_2} F(t, x(t), \dot{x}(t))dt \tag{153}$$

can be done by the Euler-Lagrange equation:

$$\frac{\partial F}{\partial x}-\frac{d}{dt}\left(\frac{\partial F}{\partial\dot{x}}\right) = -\frac{\partial V(x)}{\partial x}-\frac{d}{dt}(m\dot{x}) = -\frac{\partial V(x)}{\partial x}-m\ddot{x} = 0 \tag{154}$$

where the minimization of the action functional corresponds to the Newton's law:

$$F = m\ddot{x} \tag{155}$$

Suppose to have a function $y(x)$. When we take derivatives, we do a small change in x called dx and we see the corresponding change in y called dy, where the differential is $\frac{dy}{dx}$. On the other hand, when we are looking at variation, we are looking at the same value of x but we are looking at curves which have different slope at the same x value. The variations δy are the distance, at the same point x, between the function $y(x)$ and other functions. So, we define the operator δ operating on I for example is:

$$\delta I = \tilde{I} - I$$

This operator obeys some properties:

$$\delta dy = d\delta y$$

$$\delta \int y \, dx = \int \delta y \, dx$$

Let's take the following functional:

$$I = \int F(x, y(x), y'(x)) \, dx \tag{156}$$

$$\delta y = \tilde{y} - y \tag{157}$$

$$\delta y' = \tilde{y}' - y' \tag{158}$$

and doing the Taylor expansion:

$$F(x, y + \delta y, y' + \delta y') = F(x, y, y') + \frac{\partial F}{\partial y}\delta y + \frac{\partial F}{\partial y'}\delta y' + O(\delta^2) \tag{159}$$

Where the total variation of F is:

$$\delta^T F = F(x, y + \delta y, y' + \delta y') - F(x, y, y') = \frac{\partial F}{\partial y}\delta y + \frac{\partial F}{\partial y'}\delta y' + O(\delta^2) = \delta^1(F) + O(\delta^2) \tag{160}$$

we define also the total variation of I :

$$\delta^T I = \int_{x_1}^{x_2} F(x, y + \delta y, y' + \delta y') \, dx = \delta^1(I) + O(\delta^2) \tag{161}$$

$$\delta^1(I) = \int_{x_1}^{x_2} \delta^1(F) + O(\delta^2) = \int_{x_1}^{x_2} \left(\frac{\partial F}{\partial y}\delta y + \frac{\partial F}{\partial y'}\delta y' \right) dx \tag{162}$$

The necessary condition is that $\delta^1(I) = 0$, which means:

$$\int_{x_1}^{x_2} \left(\frac{\partial F}{\partial y} - \frac{d}{dx}\left(\frac{\partial F}{\partial y'} \right) \right) \delta y \, dx = 0 \tag{163}$$

and we get the Euler-Lagrangian equation:

$$\frac{\partial F}{\partial y} - \frac{d}{dx}\left(\frac{\partial F}{\partial y'} \right) = 0 \tag{164}$$

0.27 Free Energy Functional

The free energy is not just a function of composition, like was obtained the diffusion equation, but also to its gradient. This gradient, contributes to the free energy, which is the interficial free energy. We consider the total free energy functional:

$$F = \int_{x_1}^{x_2} f\left(x, y, z, c, \frac{\partial c}{\partial x}, \frac{\partial c}{\partial y}, \frac{\partial c}{\partial z}, \frac{\partial^2 c}{\partial x^2}, \frac{\partial^2 c}{\partial y^2}, \frac{\partial^2 c}{\partial z^2}, \frac{\partial^2 c}{\partial x \partial y}, \frac{\partial^2 c}{\partial y \partial z}, \frac{\partial^2 c}{\partial z \partial y}, ...\right) dxdydz \quad (165)$$

$$F = \int f\left(x, y, z, c, \nabla c, \nabla^2 c, ...\right) dV = \int f \, dV \quad (166)$$

Doing the Taylor expansion of (166) yields:

$$f\left(c, \nabla c, \nabla^2 c, ...\right) = f_0(c) + \frac{\partial f}{\partial(\nabla c)} \cdot \nabla c + \frac{\partial f}{\partial \nabla^2 c} : \nabla^2 c + \frac{1}{2!} \frac{\partial^2 f}{\partial \nabla c \partial \nabla c} : (\nabla c)^2 + ... \quad (167)$$

where f is a scalar, $\frac{\partial f}{\partial(\nabla c)}$ and ∇c are vectors, instead $\frac{\partial f}{\partial \nabla^2 c}, \frac{\partial^2 f}{\partial \nabla c \partial \nabla c}, (\nabla c)^2, \nabla^2 c$ are second rank tensors. We can call:

$$\frac{\partial f}{\partial \nabla c} = \frac{\partial f}{\partial\left(\frac{\partial c}{\partial x_i}\right)} = \alpha_i \quad (168)$$

$$\frac{\partial f}{\partial \nabla^2 c} = \frac{\partial f}{\partial\left(\frac{\partial^2 c}{\partial x_i \partial x_j}\right)} = \beta_{ij} \quad (169)$$

$$\frac{\partial^2 f}{\partial \nabla c \partial \nabla c} = \frac{\partial^2 f}{\partial\left(\frac{\partial c}{\partial x_i}\right) \cdot \partial\left(\frac{\partial c}{\partial x_j}\right)} = \gamma_{ij} \quad (170)$$

$$f = f_0(c) + \alpha_i (\nabla c)_i + \beta_{ij} (\nabla^2 c)_{ij} + \frac{\gamma_{ij}}{2} (\nabla c)_i (\nabla c)_j + ... \quad (171)$$

We assume that we are in a system in which there a n inversion symmetry and so $\alpha_i = 0$

$$\int \beta_{ij} \left(\nabla^2 c\right)_{ij} dV = \int \beta_{ij} \frac{\partial^2 c}{\partial x_i \partial x_j} dV = \int \beta_{ij} \frac{\partial}{\partial x_i}\left(\frac{\partial c}{\partial x_j}\right) dV \quad (172)$$

but we know that $\frac{\partial c}{\partial x_j} = (\nabla c)_j$ and so

$$\int \beta_{ij} \frac{\partial}{\partial x_i} (\nabla c)_j dV = \beta_{ij} (\nabla c)_j|_{surface} - \int \frac{\partial \beta_{ij}}{\partial x_i} (\nabla c)_j dV =$$
$$= -\int \frac{\partial}{\partial c} \beta_{ij} \frac{\partial c}{\partial x_i} (\nabla c)_j dV \quad (173)$$

where we assumed that $\beta_{ij}(\nabla c)_j|_{surface} = 0$ Substituting (173) and (171) into (167) yields:

$$F = \int \left\{ f_0(c) + \left[\frac{\gamma_{ij}}{2} - \frac{\partial \beta_{ij}}{\partial c}\right](\nabla c)_i(\nabla c)_j \right\} dV \tag{174}$$

we call $k_{ij} = \frac{\gamma_{ij}}{2} - \frac{\partial \beta_{ij}}{\partial c}$ and so:

$$F = \int \left\{ f_0(c) + k_{ij}(\nabla c)_i(\nabla c)_j \right\} dV \tag{175}$$

and since that we are assuming a cubic system, the second rank tensor is isotropic, which means $k_{ij} = k_{ji}$ and we can write:

$$F = \int \left\{ f_0(c) + k\delta_{ij}(\nabla c)_i(\nabla c)_j \right\} dV = \int \left\{ f_0(c) + k(\nabla c)_i(\nabla c)_i \right\} dV \tag{176}$$

where k is a constant. Finally the functional becomes:

$$F = \int \left\{ f_0(c) + k(\nabla c)^2 \right\} dV \tag{177}$$

we know that:

$$\frac{1}{N_V}\frac{\delta F}{\delta c} = \mu \tag{178}$$

But we know that the variational derivative is equal to the Euler-Lagrange equation:

$$\frac{\delta F}{\delta c} = \frac{\partial f_0(c)}{\partial c} - \nabla \cdot 2K(\nabla c) = \frac{\partial f_0(c)}{\partial c} - 2K\nabla^2 c \tag{179}$$

and we can write that

$$\mu N_V = \frac{\partial f_0(c)}{\partial c} - 2K\nabla^2 c \tag{180}$$

We know that the diffusion equation combined with the mass conservation is:

$$\frac{\partial c}{\partial t} = M\nabla^2 \mu \tag{181}$$

where:

$$\frac{1}{N_V}\frac{\partial c}{\partial t} = M\nabla^2\left(\frac{\partial f_0(c)}{\partial c} - 2K\nabla^2 c\right) = M\nabla^2\left(\frac{\partial f_0(c)}{\partial c}\right) - M2K\nabla^4 c \tag{182}$$

Assuming that the free energy is valid for the entire volume (we multiply it by N_V), we can write that:

$$\frac{\partial c}{\partial t} = M\nabla^2\left(\frac{\partial f_0(c)}{\partial c}\right) - M2K\nabla^4 c \tag{183}$$

This equation is called Cahn-Hilliar equation and is a modified diffusion equation. To see that is a modified diffusion equation, we can see that in 1-D:

$$\nabla \cdot \frac{\partial f_0(c)}{\partial c} = \frac{\partial}{\partial x} \cdot \frac{\partial f_0(c)}{\partial c} = \frac{\partial}{\partial c}\left(\frac{\partial f_0(c)}{\partial c}\right)\frac{\partial c}{\partial x} = \frac{\partial^2 f_0(c)}{\partial c^2}\frac{\partial c}{\partial x} = f_0''(c)\frac{\partial c}{\partial x} \tag{184}$$

Assuming that $f_0''(c) = cost$ and putting (184) into (183) yields:

$$\frac{\partial c}{\partial t} = M\,f_0''(c)\nabla^2 c - M2K\nabla^4 c = D\left(\nabla^2 c - 2K\nabla^4 c\right) \tag{185}$$

is a modification because incorporates higher order derivatives in the concentration.
Just for numerical simplicity, we will assume that:

$$f_0(c) = A\,c^2(1-c)^2 \tag{186}$$

This is valid for isothermal case, so the free energy is no longer a function of temperature but only composition. The plot is the following
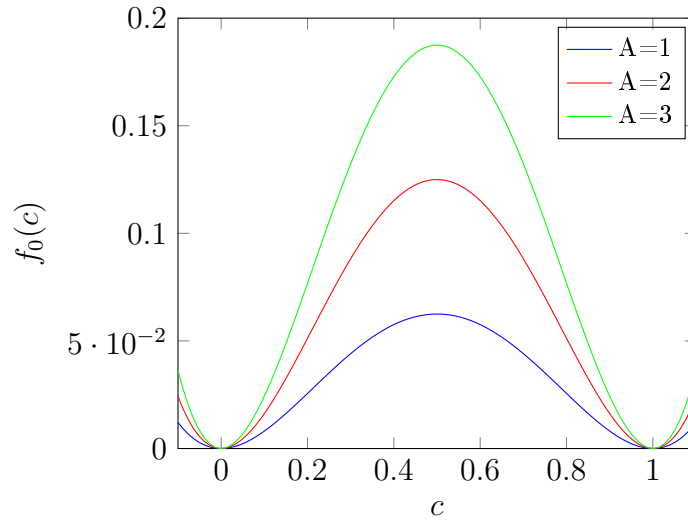

Figure 10: Plot of the function $f_0(c)$ for different A values

The first derivative of $f_0(c)$ is:

$$f'(c) = 2Ac(1-c)(1-2c) \tag{187}$$

where is equal to 0 at $c = 0, c = 1, c = \frac{1}{2}$. The second derivative is:

$$f_0''(c) = 2A(1-c)(1-2c) - 2Ac(1-2c) - 4Ac(1-c) \tag{188}$$

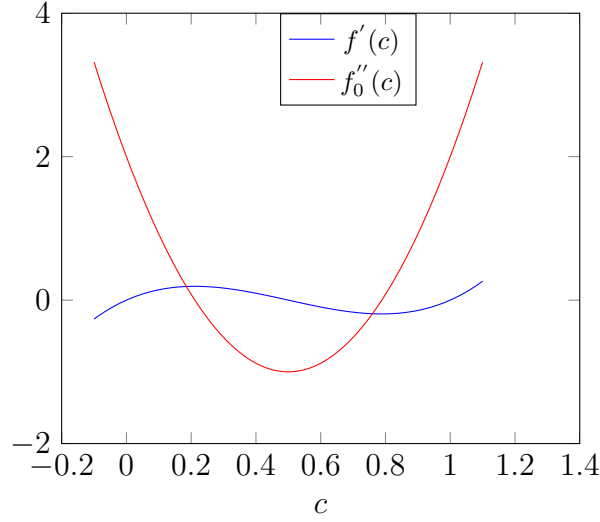where $f''(c=0) = 2A > 0, f''(c=1) = 2A > 0$ and $f''(c=0.5) = -A < 0$

44

Figure 11: Plot of the function $f'(c)$ and $f_0''(c)$ for different $A = 1$

0.28 Diffusion equation vs Cahn-Hilliard equation

The diffusion equation in 1-D is:

$$\frac{\partial c}{\partial t} = \frac{M}{N_V} f_0''(c) \frac{\partial^2 c}{\partial x^2} \tag{189}$$

and the Cahn-Hilliard equation in 1-D is:

$$\frac{\partial c}{\partial t} = \frac{M}{N_V} \left[f_0''(c) \frac{\partial^2 c}{\partial x^2} - 2K \frac{\partial^4 c}{\partial x^4} \right] \tag{190}$$

We want to put a sinusoidal variation and see what happens to that variation. We know that in the diffusion equation, the sinusoidal variation should become flat and, in the case of spinoidal decomposition, that is governed by the Cahn-Hilliard equation, that should grow. Let's take the solution of these 2 equation as follows:

$$c - c_0 = A(\beta, t)exp(i\beta x) \tag{191}$$

where $\beta = \frac{2\pi}{\lambda}$ where λ is the wave length of the composition fluctuation that we are putting. Substituting this inside the diffusion equation we get:

$$\frac{dA}{dt}exp(i\beta x) = -A\frac{M}{N_V} f_0''(c)\beta^2 exp(i\beta x) \tag{192}$$

$$\frac{dA}{dt} = -A\frac{M}{N_V}f_0^{''}(c)\beta^2 \tag{193}$$

Now substituting the solution inside (190) yields:

$$\frac{dA}{dt} = -A\frac{M}{N_V}\left[f_0^{''}(c)\beta^2 + 2K\beta^4\right] \tag{194}$$

with the solution of the two equation that is:

$$A(\beta,t) = A(\beta,0)exp(R(\beta)t) \tag{195}$$

Where for diffusion equation:

$$R(\beta) = -\frac{M}{N_V}f_0^{''}(c)\beta^2 \tag{196}$$

and for Cahn-Hilliard equation:

$$R(\beta) = -\frac{M}{N_V}\left[f_0^{''}(c)\beta^2 + 2K\beta^4\right] \tag{197}$$

Now, suppose to stay in the spinodal region where $f_0^{''}(c) < 0$, we see that in case of diffusion equation $R(\beta) > 0$, which means that for any β (any wave length small or big), the exponential is keeping growing with time instead for Cahn-Hilliard equation, in the case of large wave length (small β) we have that $\beta^2 > \beta^4$ and so $R(\beta) > 0$ but for small wave length (large β), then $\beta^2 < \beta^4$ and so $R(\beta) < 0$ which implies that there is a critical λ by which the sinusoidal decades.

1 Numerical solution Cahn-Hilliard equation with FDM

We recall the equation:

$$\frac{\partial c}{\partial t} = \frac{M}{N_V}\left[\nabla^2\left(\frac{\partial f_0(c)}{\partial c}\right) - 2K\nabla^4 c\right] \tag{198}$$

where we call

$$g(c) = \frac{\partial f_0(c)}{\partial c} = 2Ac(1-c)(1-2c) \tag{199}$$

$$\begin{aligned}
\frac{c_i^{t+\Delta t} - c_i^t}{\Delta t} &= \frac{g_{i+1}^t - 2g_i^t + g_{i-1}^t}{(\Delta x)^2} - 2K\left[\frac{c_{ww} - 4c_w + 6c_i - 4c_e + c_{ee}}{(\Delta x)^4}\right] \\
c_i^{t+\Delta t} &= c_i^t + \frac{\tilde{D}\Delta t}{(\Delta x)^2}\left(g_{i-1}^t + g_{i+1}^t - 2g_i^t\right) - \frac{2K\Delta t}{(\Delta x)^4}\left[c_{ww} - 4c_w + 6c_i - 4c_e + c_{ee}\right]
\end{aligned} \tag{200}$$

First of all we want to plot the classical diffusion equation

```
clf
clear all
dt = 0.001; %time step
dx = 1.0; %grid size
D = 1.0;
beta = D*dt/(dx*dx);
n = 32; %size of the system
N = 40000; %number of times steps

%the initial profile is sinusoidal
m = 1.0; %number of wavelenghts

for i=1:n
oldc(i)=0.5*(1.0+sin(2*pi*m*i*dx/n));
newc(i) = 0.0;
end
%plot initial profile
plot(oldc,'b');
hold on;

%start the time step loop
for j =1:N
%start the loop over nodal points to
% calculate the new composition
for i=1:n
w = i-1;
e = i+1;
if(w==0) w = w+n;
end
if(e==n+1) e = e-n;
end
newc(i) = oldc(i) + beta*(oldc(w)+oldc(e)-2*oldc(i));
end
%update the profile
for i=1:n
oldc(i) = newc(i);
end
end
plot(oldc,'r');
```
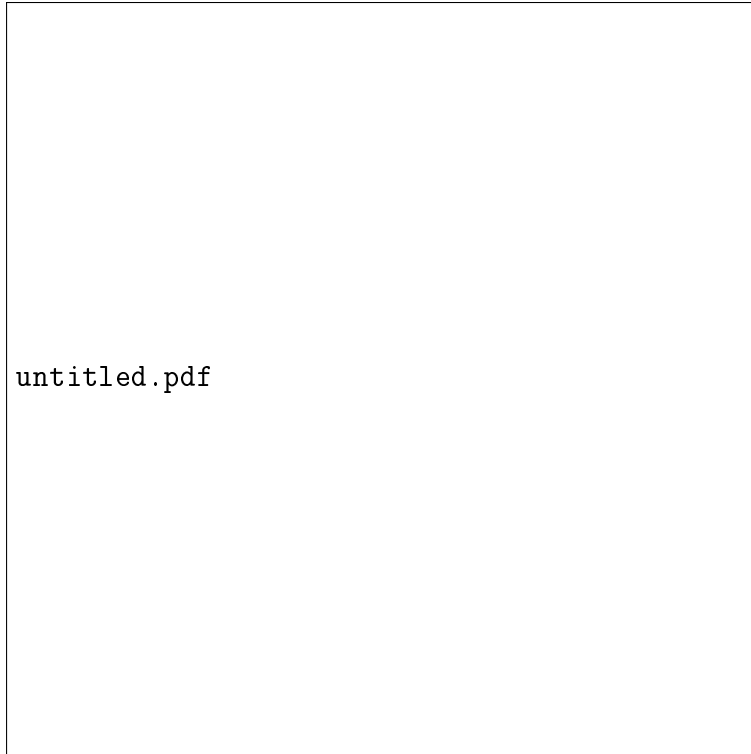
Figure 12: The blue curve is the initial condition and than the red curve is after some time, in which the sinusoidal is attenuated. After long time we will aspect an homogeneous solution at concentration 0.5

Now we want to simulate the Cahn-Hilliard equation

```
clf
clear all
dt = 0.001; %time step
dx = 1.0; %grid size
D = 1.0;
kappa = 1.0;
beta1 = D*dt/(dx*dx);
beta2 = 2*kappa*dt/(dx*dx*dx*dx);
n = 32; %size of the system
N = 40000; %number of times steps
%the initial profile is sinusoidal
m = 1.0; %number of wavelenghts
for i=1:n
oldc(i)=0.5*(1.0+sin(2*pi*m*i*dx/n));
newc(i) = 0.0;
end
%plot initial profile
plot(oldc,'b','LineWidth', 2);
hold on;
A  = 1.0;
%start the time step loop
%start the loop over nodal points to
% calculate the new composition
for i=1:n
g(i) = 2*A*oldc(i)*(1-oldc(i))*(1-2*oldc(i));
end
for j=1:N
for i=1:n
w = i-1;
ww = i-2;
e = i+1;
ee = i+2;
if(ww<1) ww = ww+n;
end
if(ee>n) ee = ee-n;
end
if(w<1) w = w+n;
end
if(e>n) e = e-n;
end
newc(i) = oldc(i) + beta1*(g(w)-2*g(i)+g(e))
```

```
−beta2 ∗( oldc (ww)−4∗oldc (w)+6∗oldc ( i )
−4∗oldc ( e)+oldc ( ee ) ) ;
end
%update the profile
for i =1:n
oldc ( i ) = newc ( i ) ;
end
end
plot ( oldc , 'r ' , 'LineWidth ' , 2 ) ;
set ( gca , 'FontName ' , 'Times New Roman ' , 'FontSize ' , 18 );
```
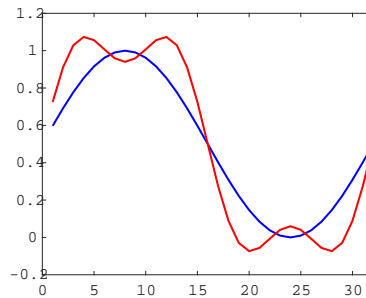

Figure 13: The blue curve is the initial condition and than the red curve is after some time, in which we have a concentration of 1 on the left, an interface and a concentration of 0 at the right. After some time we will aspect like a step function

With finite difference technique there are some problems with accuracies and since that we are taking the fourt order derivative, the error increase

2 Numerical solution Cahn-Hilliard equation with Spectral Technique

$$\frac{\tilde{c}^{t+\Delta t} - \tilde{c}^t}{\Delta t} = \tilde{D}\left(-k^2\tilde{g}\right)^t - 2Kk^4\tilde{c}^{t+\Delta t}$$

$$\tilde{c}^{t+\Delta t} = \frac{\tilde{c}^t - \tilde{D}k^2\Delta t\tilde{g}^t}{1 + 2Kk^4\Delta t}$$

(201)

This is a semi-implicit method because $(-k^2\tilde{g})$ is evaluated at time t due to the fact that at the time $t + \Delta t$ we do not know the concentration instead the other term can be calculated at time $t + \Delta t$.

First of all we plot the classical diffusion equation

```
clf
clear all
N = 32;
dx = 1.0; %grid size
m = 1.0;
for i=1:N
c(i) = 0.5*(1+sin(2*pi*m*i*dx/N));
end
%plot initial profile
plot(c,'b','LineWidth', 2);
hold on;
halfN = N/2;
delk = 2*pi/N;
dt = 0.5;
for m = 1:80
chat = fft(c);
for i=1:N
if((i-1)<=halfN) k = (i-1)*delk;
end
if((i-1)>halfN) k = (i-1-N)*delk;
end
k2 = k*k;
chat(i) = chat(i)/(1+k2*dt);
end
c = real(ifft(chat));
end
plot(c,'r','LineWidth', 2);
set(gca, 'FontName', 'Times New Roman', 'FontSize', 16)
saveas(gcf,'untitled3.pdf')
```
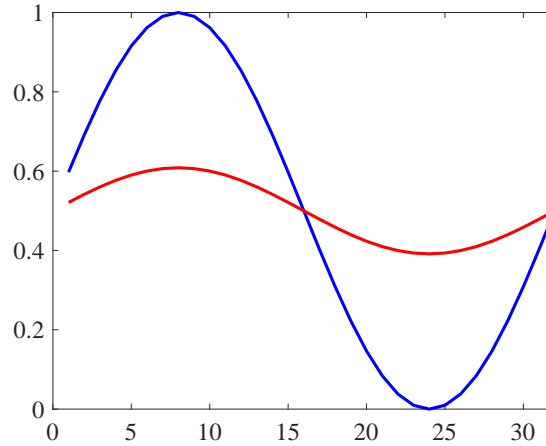
Figure 14: The blue curve is the initial condition and than the red curve is after some time, in which we have a concentration of 1 on the left, an interface and a concentration of 0 at the right. After some time we will aspect like a step function

Now, we solve the Cahn-Hilliard equation:

```
clf
clear all
N = 32; %size of the system
dx = 1.0; %grid size
m = 1.0; %number of wavelenghts
for i=1:N
c(i) = 0.5*(1+sin(2*pi*m*i*dx/N));
end
%plot initial profile
plot(c,'b','LineWidth', 2);
hold on;
halfN = N/2;
delk = 2*pi/N;
dt = 0.5;
for m = 1:80
g = 2.*c.*(1.-c).*(1.-2.*c);
ghat = fft(g);
chat = fft(c);
for i=1:N
if((i-1)<=halfN) k = (i-1)*delk;
end
if((i-1)>halfN) k = (i-1-N)*delk;
end
k2 = k*k;
```

```
k4 = k2*k2;
chat(i) = (chat(i)-dt*k2*ghat(i))/(1+2*k4*dt);
end
c = real(ifft(chat));
end
plot(c,'r','LineWidth', 2);
set(gca, 'FontName', 'Times New Roman', 'FontSize', 16)
saveas(gcf,'untitled4.pdf')
```
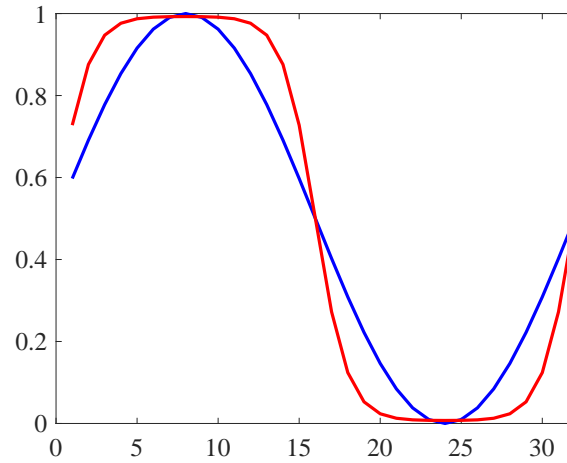

Figure 15: Case of $m = 1$ which means wavelength equal to 32

This behaviour is not valid for all wavelengths, in fact, in the following plot is showed a case where $m = 4$ that means shortest wavelength
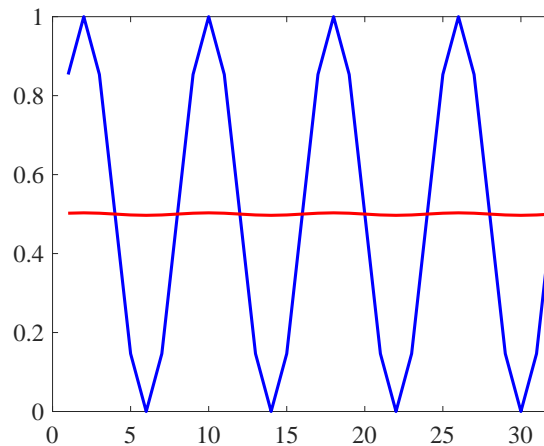

Figure 16: Case of $m = 4$ which means wavelength equal to 8

3   Analytical solution of the Cahn-Hilliard equation

We want to solve the Cahn-Hilliard equation in 1-D. The free eenrgy functional is:

$$\frac{\mathcal{F}}{N_V} = \int \left\{ f_0(c) + K(\nabla c)^2 \right\} dV \tag{202}$$

where in 1-D case becomes:

$$\frac{\mathcal{F}}{N_V} = \int \left\{ f_0(c) + K \left(\frac{dc}{dx} \right)^2 \right\} dx \tag{203}$$

where the function is:

$$f_0(c) = Ac^2(1-c)^2 \tag{204}$$

We know that the free energy for the mechanical mixture (the common tangent), can be written as:

$$\mu_B c_\beta^e + (1 - c_\alpha^e) \, \mu_A \tag{205}$$

Where c_α^e and c_β^e are the concentration of substance B in the bulk phase (equilibrium) α and β respectively. Since that $c_\alpha^e = 1$ and $c_\beta^e = 0$ which totaly is equal to 0. Since that the total free eenrgy is equal to the free energy in the phase α, plus the free energy in the phase β plus the free energy at the interface α, β, the interficial energy per atoms is obtained subtracting (205) from the total free energy:

$$\sigma = \int \left\{ f_0(c) + K \left(\frac{dc}{dx} \right)^2 \right\} dx \tag{206}$$

The system would prefer the lowest interracial energy and so we have to minimize the functional (206). Before do it, we want to slight modify the Euler-Lagrange equation. We remember that the E-L eq. is:

$$\frac{\partial F}{\partial y} - \frac{d}{dx} \left(\frac{\partial F}{\partial y'} \right) = 0 \tag{207}$$

if $F(x, y, y')$. In our case we have that $y = c$ and $y' = \frac{dc}{dx}$ and the equation becomes:

$$\frac{\partial F}{\partial c} - \frac{d}{dx} \left(\frac{\partial F}{\partial c'} \right) = 0 \tag{208}$$

A special case can be seen if F is not an explicit function of x that is our case because:

$$F = f_0(c) + k \left(\frac{dc}{dx} \right)^2 \tag{209}$$

The modification of the Euler-Lagrange equation is done as follows: Multiply by y' (207) to get:

$$y'\frac{\partial F}{\partial y} - y'\frac{d}{dx}\left(\frac{\partial F}{\partial y'}\right) = 0 \tag{210}$$

(207) implies that:

$$\frac{\partial F}{\partial y} - \frac{d}{dx}\left(\frac{\partial F}{\partial y'}\right) = 0 \Rightarrow \frac{\partial F}{\partial y} = \frac{d}{dx}\left(\frac{\partial F}{\partial y'}\right) \tag{211}$$

Let consider the following derivative:

$$\frac{d}{dx}\left(y'\frac{\partial F}{\partial y'}\right) = y'\frac{d}{dx}\left(\frac{\partial F}{\partial y'}\right) + y''\frac{\partial F}{\partial y'} \tag{212}$$

but using (211) we can write:

$$\frac{d}{dx}\left(y'\frac{\partial F}{\partial y'}\right) = y'\frac{\partial F}{\partial y} + y''\frac{\partial F}{\partial y'} \tag{213}$$

we know that if $F(x, y(x), y'(x))$, the total derivative of F is:

$$\frac{dF}{dx} = \frac{\partial F}{\partial x} + y'\frac{\partial F}{\partial y} + y''\frac{\partial F}{\partial y'} \tag{214}$$

and if if F is not an explicit function of x, the first term of (214) is 0 and we get:

$$\frac{d}{dx}\left(y'\frac{\partial F}{\partial y'}\right) = \frac{dF}{dx} \tag{215}$$

$$\frac{d}{dx}\left(y'\frac{\partial F}{\partial y'} - F\right) = 0 \Rightarrow y'\frac{\partial F}{\partial y'} - F = \alpha \tag{216}$$

where α is a constant. We know that in the bulk region F and $\frac{\partial F}{\partial y'}$ should be 0 becuase we have the bulk concentration and the profile is flat there, but since that α is a constant, should be 0 every where and so the equation to solve is:

$$y'\frac{\partial F}{\partial y'} - F = 0 \tag{217}$$

$$\frac{dc}{dx}\frac{\partial F}{\partial\left(\frac{dc}{dx}\right)} - F = 0 \tag{218}$$

with the assumption that

$$F = Ac^2(1-c)^2 + K\left(\frac{dc}{dx}\right)^2 \tag{219}$$

$$\frac{\partial F}{\partial\left(\frac{dc}{dx}\right)} = 2K\frac{dc}{dx} \tag{220}$$

$$2K\left(\frac{dc}{dx}\right)^2 - Ac^2(1-c)^2 - K\left(\frac{dc}{dx}\right)^2 = 0 \tag{221}$$

$$K\left(\frac{dc}{dx}\right)^2 - Ac^2(1-c)^2 = 0 \tag{222}$$

$$\left(\frac{dc}{dx}\right)^2 = \frac{A}{K}c^2(1-c)^2 \tag{223}$$

where $\beta = \sqrt{\frac{A}{K}}$, and so:

$$\frac{dc}{dx} = \beta c(1-c) \tag{224}$$

$$\frac{dc}{c(1-c)} = \beta dx \tag{225}$$

$$\frac{1}{c(1-c)} = \frac{A}{c} + \frac{B}{(1-c)} \tag{226}$$

$$\begin{aligned}
\frac{A}{c} + \frac{B}{(1-c)} &= \frac{1}{c(1-c)} \\
\frac{A - Ac + Bc}{c(1-c)} &= \frac{1}{c(1-c)} \\
A = 1; \quad B - A &= 0 \Rightarrow B = 1 \\
\frac{dc}{c} + \frac{dc}{(1-c)} &= \beta dx \\
\frac{dc}{c} - \frac{(-dc)}{(1-c)} &= \beta dx \\
\ln(c) - \ln(1-c) &= \beta x \\
\ln\left(\frac{c}{1-c}\right) &= \beta dx \\
\frac{1-c}{c} = e^{-\beta x} \Rightarrow \frac{1}{c} - 1 &= e^{-\beta x} \Rightarrow \frac{1}{c} = 1 + e^{-\beta x}
\end{aligned} \tag{227}$$

$$c = \frac{1}{1 + e^{-\beta x}} = \frac{e^{\beta x}}{1 + e^{\beta x}} \tag{228}$$

The following solution can be written also in another way. We know that:

$$\tanh(x) = \frac{e^x - e^{-x}}{e^x + e^{-x}} = \frac{1 - e^{-2x}}{1 + e^{-2x}}$$

$$\tanh(x) + 1 = 1 + \frac{1 - e^{-2x}}{1 + e^{-2x}} = \frac{1 + e^{-2k} + 1 - e^{-2x}}{1 + e^{-2x}}$$

$$\frac{1 + \tanh(x)}{2} = \frac{1}{1 + e^{-2x}}$$

$$\frac{1}{1 + e^{-2x}} = \frac{1}{2}(1 + \tanh(x))$$

(229)

and finally we get the solution in term of hyperbolic tangent:

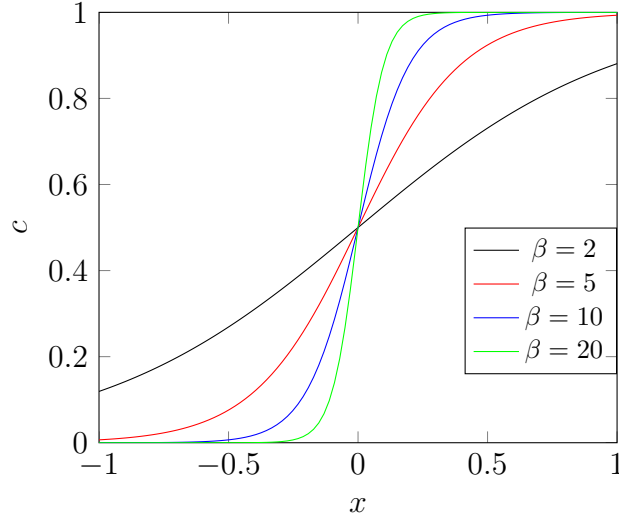$$c = \frac{1}{2}\left(1 + \tanh\left(\frac{\beta x}{2}\right)\right)$$

(230)

Figure 17: Plot of the function $f'(c)$ and $f_0''(c)$ for different $A = 1$

4   Interfacial energy

Using (222) and placing into (206), we can write the interfacial energy as:

$$\sigma = 2 \int_{-\infty}^{\infty} f_0(c)dx \tag{231}$$

we know that $f_0(c)$ is a function of c and the integral is over x. We want to change x with c. We know that at $x = -\infty \to c = 0$ and at $x = \infty \to c = 1$. We know that

$$\frac{f_0(c)}{K} = \left(\frac{dc}{dx}\right)^2 \Rightarrow \frac{dc}{dx} = \left(\frac{f_0(c)}{K}\right)^{1/2} \Rightarrow dx = \left(\frac{K}{f_0(c)}\right)^{1/2} dc \tag{232}$$

and the interfacial energy becomes:

$$\sigma = 2 \int_0^1 (f_0(c)K)^{1/2}dc = 2 \int_0^1 (A K c^2(1-c)^2)^{1/2}dc = 2\gamma \int_0^1 c(1-c)dc \tag{233}$$

where the solution is:

$$\sigma = \frac{\gamma}{3} \quad , \quad \gamma = (A K)^{1/2} \tag{234}$$

# 5   Order-disorder transition and Allen-Cahn equation

Ordering transcends the crystalline arrangement, exemplified succinctly through a specific coordinate system termed as "b2 ordered," notably observed within the nickel-aluminum system. When considering a composition equating to equal atomic percentages of nickel and aluminum (roughly 50% each), examining the phase diagram reveals a cubic structure forming within nickel-aluminum. While both nickel and aluminum individually adopt a face-centered cubic (FCC) structure, the compound NiAl assumes a distinct B2 structure characterized by ordered body-centered cubic (BCC) arrangement.

This concept of "ordered BCC" denotes a scenario where, within a BCC system comprising two distinct atom types, such as red and blue atoms, specific lattice positions are preferentially occupied. In a conventional crystalline lattice, these positions—eight cube corners and a singular body-centered position—are randomly filled, allowing any site to host either a red or blue atom. However, in an ordered BCC structure, atoms exhibit a distinct preference; for instance, red atoms exclusively occupy the body-centered position, while blue atoms solely occupy the cube corners. This delineates one variant of ordering, with another variant involving the reverse configuration, where cube corners are occupied by red atoms and the body center by blue atoms.
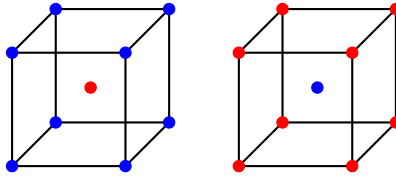
In this context, nickel atoms, for instance, may be represented as red, displaying a preference to be surrounded by blue aluminum atoms, while aluminum atoms exhibit a preference for neighboring nickel atoms. Regarding the energetics, in the scenario of spinodal, when omega exceeds 0 (positivity), it indicates that the energy of the AB interaction (E_{AB}) surpasses the average energies of AA (E_{AA}) and BB(E_{BB}). Conversely, in the case of ordering, when omega is less than zero, it signifies a preference for ordered arrangements.

Now consider the system in which every point is a unit cell for example. We will mark with red arrow a region in which the red atom is at the center and with a blue arrow a region in which the blue atom is at the center. These two zones are nown as domains.
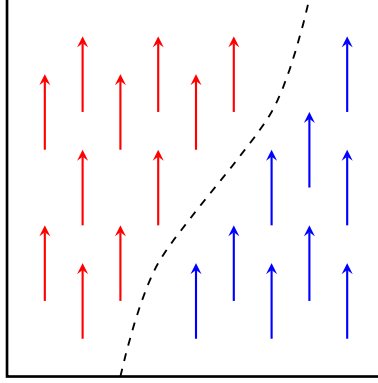
As can be seen it is formed a domain wall (dotted line) which has hich energy. Spinodal decomposition was described using composition where composition isna conservabel variable which should be respected the condition that:

$$\frac{d}{dt} \int c\, dx = 0 \tag{235}$$

On the other hand, when we have the ordered domain, as in the picture, it is also possible that the red arrows changes in such way the blue atoms come to the center. In this case we call the ϕ the ordered parameter when for red zone is equal to 0 and for the blue zone is equal to 0. Across the wall goes like the hyperbolic tangent that was found in the previous derivation. The functional is similar:

$$\mathcal{F} = \int \left\{ f_0(\phi) + K(\nabla\phi)^2 \right\} dV \tag{236}$$

I can take the variational derivative of this functional with respect to the ϕ parameter to get the chemical potential

$$\frac{\delta \mathcal{F}}{\delta \phi} = \mu \tag{237}$$

In the case of Cahn-Hilliard equation, the flux is proportional to gradient in chemical potential and there was mass conservation. Here instead there is no conservation in the sense that we can start maybe with 50% of blue and red atoms at the center and we can arrive to

100% of blue atoms at the center or v100% of red atoms at the center. The constitutive law is:

$$\frac{\partial \phi}{\partial t} = -L\mu \tag{238}$$

and this is known as the Allen-Cahn equation where in our case becomes:

$$\frac{\partial \phi}{\partial t} = -L\left(\frac{\partial f_0(\phi)}{\partial \phi} - 2K\nabla^2\phi\right) \tag{239}$$

$$\frac{\partial \phi}{\partial t} = 2KL\nabla^2\phi - L\frac{\partial f_0(\phi)}{\partial \phi} \tag{240}$$

$$g(\phi) = \frac{\partial f_0(\phi)}{\partial \phi} = 2A\phi(1-\phi)(1-2\phi)$$

This is called also Reaction-Diffusion equation.

6 Numerical Solution Allen-Cahn equation

We want to do the Fourier transform:

$$\frac{\tilde{\phi}^{t+\Delta t} - \tilde{\phi}^t}{\Delta t} = -2KLk^2\phi^{t+\Delta t} - L\tilde{g}^t$$
$$\tilde{\phi}^{t+\Delta t} = \frac{\tilde{\phi}^t - L\Delta t\tilde{g}^t}{1 + 2KLk^2} \tag{241}$$

```
clear all
clc
clf
kappa=1.0;
L=1.0;
A=1.0;
N=128;
DX=1.0;
phi=zeros(N,1);
for i=(N/4)+1:3*N/4
phi(i)=1.0;
end
plot(phi,'r','LineWidth', 2);
hold on;
halfN=N/2;
delk=2*pi/N;
```

```
dt=0.5;
for m=1:400
g=2*A.*phi.*(1.-phi).*(1.-2.*phi);
ghat=fft(g);
phihat=fft(phi);
for i=1:N
if((i-1)<= halfN) k=(i-1)*delk;
end
if((i-1)>halfN) k=(i-1-N)*delk;
end
k2=k*k;
phihat(i)=(phihat(i)-L*dt*ghat(i))/(1+2*kappa*L*dt*k2);
end
phi=real(ifft(phihat));
end
plot(phi,'b','LineWidth', 2);
set(gca, 'FontName', 'Times New Roman', 'FontSize', 18);
```
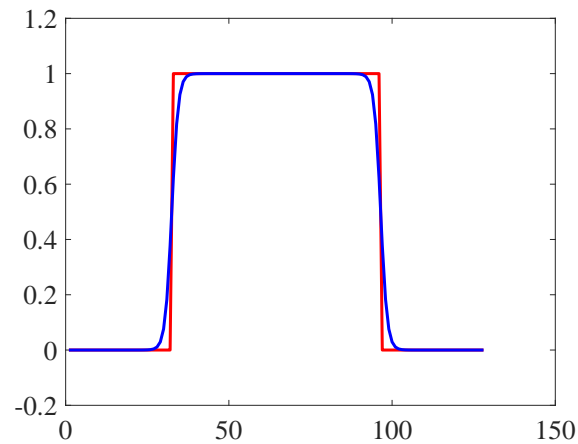

Figure 18: The blue curve is the initial condition and than the red curve is after some time

7 Spinodal decomposition in 2D

Let us consider a system which is undergoing spinoidal decomposition. Initially the composition in the system is uniform everywhere. Take a alloy at a certain composition c_0. The order parameter is the one that describe the micro-structure in the system and the first step should be to identify it, where in this case is composition. The second step is the thermodynamics, we want to write the free energy functional, because the free energy is a function of composition and its gradient $G(c, \nabla c)$. The step three is to write down the phase-field equation (evolution equation). Since that the c is the conserve-ordered parameter, we will use the Cahn-Hilliard equation. The step four is to solve the equation in 2D.

We know that in 2D:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \tag{242}$$

When we do the period boundary condition implementation, we are assuming that the micro structure that we are considering is a Representative Volume Element (RVE), which means that the region that we are looking is a representative area of the entire micro structure. The Fourier transform implementation in 2D is:

$$
\begin{aligned}
\frac{\partial \tilde{c}}{\partial t} &= -M\left(k_x^2 + k_y^2\right)\tilde{g}^t - 2KM\left(k_x^2 + k_y^2\right)^2 \tilde{c}^{t+\Delta t} \\
\tilde{c}^{t+\Delta t}\left(1 + 2KM\left(k_x^2 + k_y^2\right)^2 \Delta t\right) &= \tilde{c}^t - M\left(k_x^2 + k_y^2\right)\Delta t \tilde{g}^t \\
\tilde{c}^{t+\Delta t} &= \frac{\tilde{c}^t - M\left(k_x^2 + k_y^2\right)\Delta t \tilde{g}^t}{1 + 2KM\left(k_x^2 + k_y^2\right)^2 \Delta t}
\end{aligned}
\tag{243}
$$

```
clear all
clc
clf
more off %it will show all figures like a video
Nx=64;
Ny=64;
for i=1:Nx
for j=1:Ny
c(i,j)=0.5+0.1*(0.5-rand());
end
end
colormap(jet(256));
contourf(c,200,'LineColor','none')
view(2);
pause(0);
dt=0.5;
```

```matlab
halfNx=Nx/2;
halfNy=Ny/2;
delkx=2*pi/Nx;
delky=2*pi/Ny;
A=1.0;
M=1.0;
kappa=1.0;
for m=1:100
for n=1:10
g=2.*A.*c.*(1.-c).*(1.-2.*c);
ghat=fft2(g);
chat=fft2(c);
for i=1:Nx
if((i-1)<=halfNx) kx=(i-1)*delkx;
end
if((i-1)>=halfNx) kx=(i-1-Nx)*delkx;
end
for j=1:Ny
if((j-1)<=halfNy) ky=(j-1)*delky;
end
if((j-1)>=halfNy) ky=(j-1-Ny)*delky;
end
k2=kx*kx+ky*ky;
k4=k2*k2;
chat(i,j)=(chat(i,j)-M*dt*k2*ghat(i,j))/(1.+2*M*kappa*k4*dt);
end
end
c=real(ifft2(chat));
end
colormap(jet(256));
contourf(c,200,'LineColor','none')
view(2);
pause(0);
end
set(gca, 'FontName', 'Times New Roman', 'FontSize', 18);
```

8 Gibbs Thomson effect

Gibbs Thomson effect is a curvature effect (also called capillary effect). It is the effect of equilibrium in system because of interfacial energy. For example, if we have solid-liquid in contact with each other at their melting temperature, this temperature is that one in which solid and liquid are in equilibrium. The melting temperature is for a solid-liquid interface that is separated by a planar boundary. The melting temperature is different if we have a curved interface. The planar surface has a energy lower respect to the curved one.
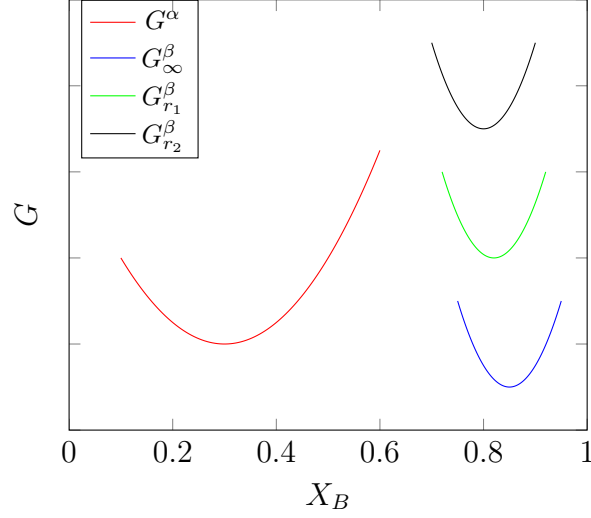
Let us take an example in which we have one big beta precipitate of radius r_1 and one small precipitate of radius r_2, in a alpha matrix. We want to find the composition of alpha phase in between the two precipitate. Sending a common tangent of G^α and the other parabolas we can see that $c_{r_2}^\alpha > c_{r_1}^\alpha$ which means that there is a concentration gradient in between, that implies the movement of atoms from the zone close to the small precipitate to the big precipitate, that implies the small precipitate will shrink to maintain the composition to outside constant and instead the diffusion will make the big precipitate much bigger.
The change in composition for the alpha phase is:

$$\Delta c_\alpha = \frac{\gamma k}{r(c_\beta^e - c_\alpha^e)\chi_\alpha} \tag{244}$$

where $\chi_\alpha = \frac{\partial^2 f}{\partial c^2}|_\alpha$

Let us consider a binary alloy $(A - B)$ and we want to look a the micro-structure. The matrix is $\alpha - A$ rich matrix and we have some precipitates. The two precipitate are of different type β_1 and β_2 where both are $B-$ rich. Let us say that β_1- crystal structure is not the same as β_2- structure. If this happens, we need two ordered parameters, one is composition c to referred to α/β phase and ϕ to referred to crystal structure. We are going to put together the A-C and C-H equation.

9 Precipitate Growth

There could be another scenario in which there are classical growth theories for a precipitate growth, one of them is due to Zener-Frank. Suppose if we have a supersaturated $\alpha-$ matrix (means that it has more B then what equilibrium α would need) and suppose to have an isolated precipitate of β growing out of the matrix. They came up with a the expression for the growth rate of such precipitate in 1D, 2D and 3D systems. The other assumption was to assume a constant diffusivity D and no Gibbs Thomson effect. The last assumption is well posed for a $1D$ case but in 2D and 3D we have a curvature and that effect is important. Also here we need two ordered parameter c and ϕ, even if α and β have the same crystal structure. We introduce ϕ just to see if the diffusivity remains constant. We know that D is related by:

$$D = M \frac{\partial^2 f}{\partial c} \tag{245}$$

$$f = A\,c^2(1-c)^2 \tag{246}$$

$$\frac{\partial f}{\partial c} = 2A\,c(1-c)(1-2c) \tag{247}$$

$$\frac{\partial^2 f}{\partial c^2} = 2A(1-c)(1-2c) - 2A\,c(1-2c) - 4A\,c(1-c) \tag{248}$$

Let us assume that we are considering a planar interfce growth (we are lookig at 1D problem). The free energy expression is:

$$\frac{\mathcal{F}}{N_V} = \int \left\{ f(c,\phi) + K_c(\nabla c)^2 + K_\phi(\nabla \phi)^2 \right\} dV \tag{249}$$

where we choose:

$$f(c,\phi) = A\,c^2(1 - W(\phi)) + B(1-c)^2 W(\phi) + P\phi^2(1-\phi^2) \tag{250}$$

with the function:

$$W(\phi) = \begin{cases} 0 & \phi \leq 0 \\ \phi^3(10 - 15\phi + 6\phi^2) & 0 \leq \phi \leq 1 \\ 1 & \phi > 1 \end{cases}$$
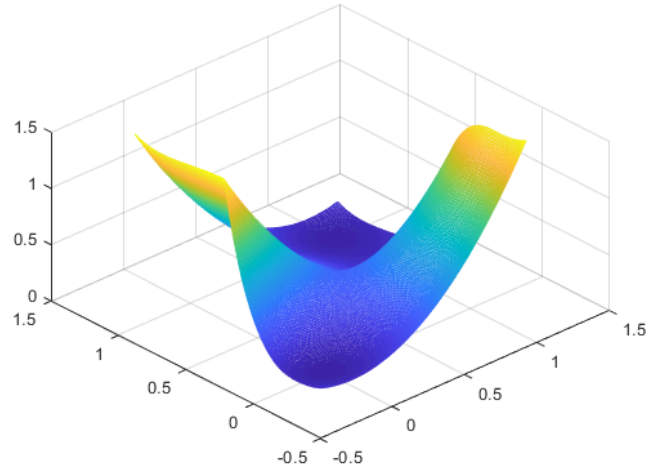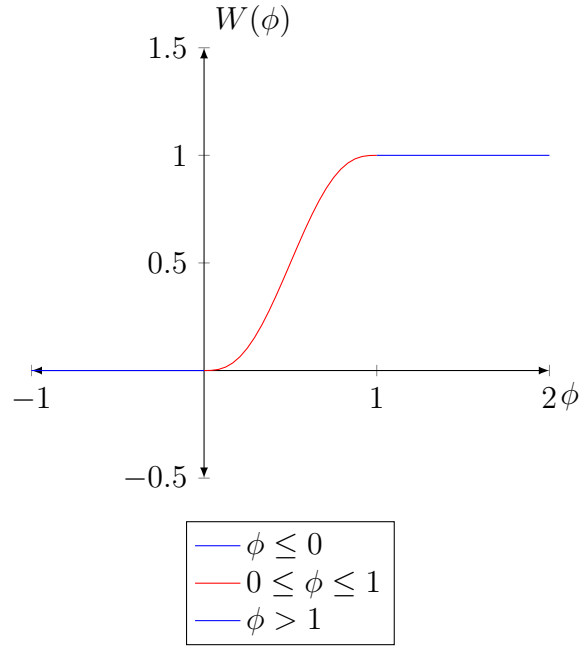
Figure 19: Plot of the function $f(c, \phi)$

This is done because if we choose the function f as a quadratic, then the second derivative respect to concentration is a function of concentration and this does not guarantied a constant diffusivity.

The Cahn-Hilliard equation is:

$$\frac{\partial c}{\partial t} = M\nabla^2 \left(\frac{\delta \left(\mathcal{F}/N_v \right)}{\delta c} \right) \tag{251}$$

66

and the Alen-Cahn equation is:

$$\frac{\partial \phi}{\partial t} = -L\left(\frac{\delta\left(\mathcal{F}/N_v\right)}{\delta\phi}\right) \tag{252}$$

where

$$\frac{\delta\left(\mathcal{F}/N_v\right)}{\delta c} = \frac{\partial f(c,\phi)}{\partial c} - 2K_c\nabla_c^2$$
$$\frac{\delta\left(\mathcal{F}/N_v\right)}{\delta\phi} = \frac{\partial f\left(c_i\phi\right)}{\partial\phi} - 2K_\phi\nabla^2\phi \tag{253}$$

Let us define the following functions:

$$h_c = \frac{\partial f\left(c_i\phi\right)}{\partial c} = 2A\,c(1 - W(\phi)) - 2B(1 - c)W(\phi)$$
$$h_\phi = \frac{\partial f(c,\phi)}{\partial\phi} = -Ac^2W'(\phi) + B(1 - c)^2W(\phi) + 2P\phi(1 - \phi)(1 - 2\phi) \tag{254}$$

where

$$W'(\phi) = \begin{cases} 0 & \phi < 0 \\ 3\phi^2\left(10 - 15\phi - 16\phi^2\right) + \phi^3(12\phi - 15) & 0 \le \phi \le 1 \\ 0 & \phi > 1 \end{cases}$$

anf finally the two equations become:

$$\frac{\partial c}{\partial t} = M\nabla^2\left(h_c(c,\phi) - 2K_c\nabla^2 c\right)$$
$$\frac{\partial\phi}{\partial t} = -L\left(h_\phi\left(c,\phi\right) - 2K_\phi\nabla^2\phi\right) \tag{255}$$

Both of these equation will ve solved using a Semi-implicit spectral technique

```
function y=f(x)
y=x*x*x*(10-15*x+6*x*x);
end
function y=fp(x)
y=3*x*x*(10-15*x+6*x*x) + x*x*x*(12*x-15);
end
clear all
clc
clf
more off
N=64;
halfN=N/2;
R=10;
for i=1:N
for j=1:N
if(((i-halfN)*(i-halfN)+(j-halfN)*(j-halfN)<R*R))
c(i,j)=1.0;
phi(i,j)=1.0;
else
c(i,j)=0.02;
phi(i,j)=0.0;
end
end
end
Cprofile=c(:,halfN);
Phiprofile=phi(:,halfN);
hold on;
plot(Cprofile,'r','LineWidth', 2);
plot(Phiprofile,'b','LineWidth', 2);
hold off;
delk=2*pi/N;
dt=0.5;
A=1.0;
B=1.0;
P=1.0;
M=1.0;
kappac=1.0;
kappaphi=1.0;
%for time loop
for m=1:1
for n=1:100
%for position loop
```

```
for i=1:N
for j=1:N
W=f(phi(i,j));
if(phi(i,j)<0) W=0;
elseif (phi(i,j)>1) W=1;
end
hc(i,j)=2*A*c(i,j)*(1-W)-2*B*(1.-c(i,j))*W;
end
end
for i=1:N
for j=1:N
Wp=fp(phi(i,j));
if(phi(i,j)<0) Wp=0;
elseif (phi(i,j)>1) Wp=0;
end
hphi(i,j)=-A*c(i,j)*c(i,j)*Wp+2*B*(1.-c(i,j))*(1-c(i,j))*Wp
+2*P*phi(i,j)*(1-phi(i,j))*(1-2*phi(i,j));
end
end
hchat=fft2(hc);
hphihat=fft2(hphi);
chat=fft2(c);
phihat=fft2(phi);
for i=1:N
for j=1:N
if((i-1)<=halfN) kx=(i-1)*delk;
end
if((i-1)>halfN) kx=(i-N-1)*delk;
end
if((j-1)<=halfN) ky=(j-1)*delk;
end
if((j-1)>halfN) ky=(j-N-1)*delk;
end
k2=kx*kx+ky*ky;
k4=k2*k2;
chat(i,j)=(chat(i,j)-dt*k2*hchat(i,j))/(1+2*k4*dt);
phihat(i,j)=(phihat(i,j)-dt*hphihat(i,j))/(1+2*k2*dt);
end
end
c=real(ifft2(chat));
phi=real(ifft2(phihat));
end
```

```
end
Cprofile=c(:,halfN);
Phiprofile=phi(:,halfN);
hold on;
plot(Cprofile ,'r','LineWidth', 2);
plot(Phiprofile ,'b','LineWidth', 2);
hold off;
set(gca, 'FontName', 'Times New Roman', 'FontSize', 18);
```
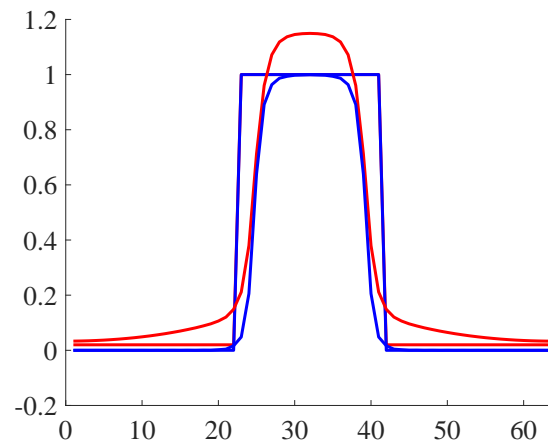

Figure 20

10   Grain growth: Fan-Chen model

If we look the micro-structure, we will see a lot of grains. Each grain represent the orientation of the unit cell, in that region, respect to a reference frame. Each orientation is denoted with a different number. The ordered parameter that must be used is called η_i, with $i = 1, 2, ..., p$. In a certain region, the corresponding unit parameter will be 1 and the rest, outside that region, is 0. This order parameter represent the orientation of the crystallizes with respect to same external reference frame.

We can also think of a vector order parameter. When there are region in which we have a gradient in η_i, that region is where we have a grain boundary.

We know that ae the end for example, any one of the total grains can actually eat up all the other grains and become a single orientation. We need minima for each η_i. The bulk free energy density f_0, should be the same for all η_i. There is a particular bulk free energy density given by Fan-Chen that is:

$$f_0(\eta_1, \eta_2, ..., \eta_p) = \sum_{i=1}^{p} -\frac{\alpha \eta_i^2}{2} + \frac{\beta \eta_i^4}{4} + \gamma \sum_{i=1}^{p} \sum_{j \neq i}^{p} \eta_i^2 \eta_j^2 \tag{256}$$

There are $2p$ minima and they are at $\eta_i = \pm 1$ and at $\eta_{i \neq j} = 0$. We want to restrict the order parameter just on the positive side. We should guarantide that $\gamma > \frac{\beta}{2}$. The free energy is:

$$\mathcal{F} = \int \left\{ f_0(\eta_1, \eta_2, ..., \eta_p) + \sum_{i=1}^{p} K_i (\nabla \eta_i)^2 \right\} dV \tag{257}$$

we can assume that all K_i are the same. For each i we need to write p coupled evolution equations:

$$\frac{\partial \eta_i}{\partial t} = -L \left(\frac{\partial f_0}{\partial \eta_i} - 2K_i \nabla^2 \eta_i \right) \tag{258}$$

Let us call $g_i = \frac{\partial f_0}{\partial \eta_i}$. For a periodic boundary condition the discretized equation is:

$$\frac{\partial \tilde{\eta}_i}{\partial t} = -L_i \tilde{g}_i^t - 2k^2 L_i K_i \tilde{\eta}_i^{t+\Delta t}$$

$$\frac{\tilde{\eta}_i^{t+\Delta t} - \eta_i^t}{\Delta t} = -L_i \tilde{g}_i^t - 2 L_i K_i k^2 \eta_i^{t+\Delta t} \tag{259}$$

$$\eta_i^{t+\Delta t} = \frac{\eta_i^t - L_i \Delta t \tilde{g}_i^t}{1 + 2 L_i K_i k^2 \Delta t}$$

Let us assume to have 6 different orientation. In the initial state, we have a random orientation for each side given.

```
clear all
clc
clf
more off;
p=6;
kappa1=1.0;
kappa2=1.0;
kappa3=1.0;
kappa4=1.0;
kappa5=1.0;
kappa6=1.0;
L1=1.0;
L2=1.0;
L3=1.0;
L4=1.0;
L5=1.0;
L6=1.0;
alpha=1.0;
beta=1.0;
gamma=1.0;
N=64;
dx=1.0;
%uniform discrete random n. generation
phi=unidrnd(6,N,N);
eta1=zeros(N,N);
eta2=zeros(N,N);
eta3=zeros(N,N);
eta4=zeros(N,N);
eta5=zeros(N,N);
eta6=zeros(N,N);
for i=1:N
for j=1:N
if((phi(i,j)==1)) eta1(i,j)=1.0;
elseif((phi(i,j)==2)) eta2(i,j)=1.0;
elseif((phi(i,j)==3)) eta3(i,j)=1.0;
elseif((phi(i,j)==4)) eta4(i,j)=1.0;
elseif((phi(i,j)==5)) eta5(i,j)=1.0;
elseif((phi(i,j)==6)) eta6(i,j)=1.0;
end
end
```

```
end
for k=1:N
for l=1:N
b(k,l)=eta1(k,l)*(eta2(k,l)+eta3(k,l)+eta4(k,l)+eta5(k,l)+eta6(k,l))...
+eta2(k,l)*(eta3(k,l)+eta4(k,l)+eta5(k,l)+eta6(k,l))+...
eta3(k,l)*(eta4(k,l)+eta5(k,l)+eta6(k,l))...
+eta4(k,l)*(eta5(k,l)+eta6(k,l))+eta5(k,l)*eta6(k,l);
end
end
colormap(jet(256));
contourf(b,200,'LineColor','none')
view(2);
pause(0);
halfN=N/2;
delk=2*pi/N;
dt=0.5;
for n=1:30 %number of total time steps
for m=1:2 %I look the microstruc. after m time steps
for j=1:N
for k=1:N
g1(j,k)=-eta1(j,k)+eta1(j,k)*eta1(j,k)*eta1(j,k)+...
2*eta1(j,k)*(eta2(j,k)*eta2(j,k) ...
+eta3(j,k)*eta3(j,k)+eta4(j,k)*eta4(j,k)+...
eta5(j,k)*eta5(j,k)+eta6(j,k)*eta6(j,k));
g2(j,k)=-eta2(j,k)+eta2(j,k)*eta2(j,k)*eta2(j,k)+...
2*eta2(j,k)*(eta1(j,k)*eta1(j,k) ...
+eta3(j,k)*eta3(j,k)+eta4(j,k)*eta4(j,k)+...
eta5(j,k)*eta5(j,k)+eta6(j,k)*eta6(j,k));
g3(j,k)=-eta3(j,k)+eta3(j,k)*eta3(j,k)*eta3(j,k)+...
2*eta3(j,k)*(eta1(j,k)*eta1(j,k) ...
+eta2(j,k)*eta2(j,k)+eta4(j,k)*eta4(j,k)+...
eta5(j,k)*eta5(j,k)+eta6(j,k)*eta6(j,k));
g4(j,k)=-eta4(j,k)+eta4(j,k)*eta4(j,k)*eta4(j,k)+...
2*eta4(j,k)*(eta1(j,k)*eta1(j,k) ...
+eta2(j,k)*eta2(j,k)+eta3(j,k)*eta3(j,k)+...
eta5(j,k)*eta5(j,k)+eta6(j,k)*eta6(j,k));
g5(j,k)=-eta5(j,k)+eta5(j,k)*eta5(j,k)*eta5(j,k)+...
2*eta5(j,k)*(eta1(j,k)*eta1(j,k) ...
+eta2(j,k)*eta2(j,k)+eta3(j,k)*eta3(j,k)+...
eta4(j,k)*eta4(j,k)+eta6(j,k)*eta6(j,k));
g6(j,k)=-eta6(j,k)+eta6(j,k)*eta6(j,k)*eta6(j,k)+...
2*eta6(j,k)*(eta1(j,k)*eta1(j,k) ...
```

```matlab
+eta2(j,k)*eta2(j,k)+eta3(j,k)*eta3(j,k)+...
eta4(j,k)*eta4(j,k)+eta5(j,k)*eta5(j,k));
end
end
g1hat=fft2(g1);
g2hat=fft2(g2);
g3hat=fft2(g3);
g4hat=fft2(g4);
g5hat=fft2(g5);
g6hat=fft2(g6);
eta1hat=fft2(eta1);
eta2hat=fft2(eta2);
eta3hat=fft2(eta3);
eta4hat=fft2(eta4);
eta5hat=fft2(eta5);
eta6hat=fft2(eta6);
for i=1:N
for j=1:N
if ((i-1)<=halfN) kx=(i-1)*delk;
end
if ((i-1)>halfN) kx=(i-1-N)*delk;
end
if ((j-1)<=halfN) ky=(j-1)*delk;
end
if ((j-1)>halfN) ky=(j-1-N)*delk;
end
k2=kx*kx+ky*ky;
eta1hat(i,j)=(eta1hat(i,j)-L1*dt*g1hat(i,j))/(1+2*L1*kappa1*k2*dt);
eta2hat(i,j)=(eta2hat(i,j)-L2*dt*g2hat(i,j))/(1+2*L2*kappa2*k2*dt);
eta3hat(i,j)=(eta3hat(i,j)-L3*dt*g3hat(i,j))/(1+2*L3*kappa3*k2*dt);
eta4hat(i,j)=(eta4hat(i,j)-L4*dt*g4hat(i,j))/(1+2*L4*kappa4*k2*dt);
eta5hat(i,j)=(eta5hat(i,j)-L5*dt*g5hat(i,j))/(1+2*L5*kappa5*k2*dt);
eta6hat(i,j)=(eta6hat(i,j)-L6*dt*g6hat(i,j))/(1+2*L6*kappa6*k2*dt);
end
end
eta1=real(ifft2(eta1hat));
eta2=real(ifft2(eta2hat));
eta3=real(ifft2(eta3hat));
eta4=real(ifft2(eta4hat));
eta5=real(ifft2(eta5hat));
eta6=real(ifft2(eta6hat));
end
```

```
b=zeros(N,N);
for k=1:N
for l=1:N
b(k,l)=eta1(k,l)*(eta2(k,l)+eta3(k,l)+eta4(k,l)+eta5(k,l)+eta6(k,l))...
+eta2(k,l)*(eta3(k,l)+eta4(k,l)+eta5(k,l)+eta6(k,l))+...
eta3(k,l)*(eta4(k,l)+eta5(k,l)+eta6(k,l))...
+eta4(k,l)*(eta5(k,l)+eta6(k,l))+eta5(k,l)*eta6(k,l);
end
end
colormap(jet(256));
contourf(b,200,'LineColor','none')
view(2);
pause(0);
end
```