

# **Thermodynamics of diffusion**

*(extracurricular material - not tested)*

## **Driving force for diffusion**

Diffusion in ideal and real solutions

Thermodynamic factor

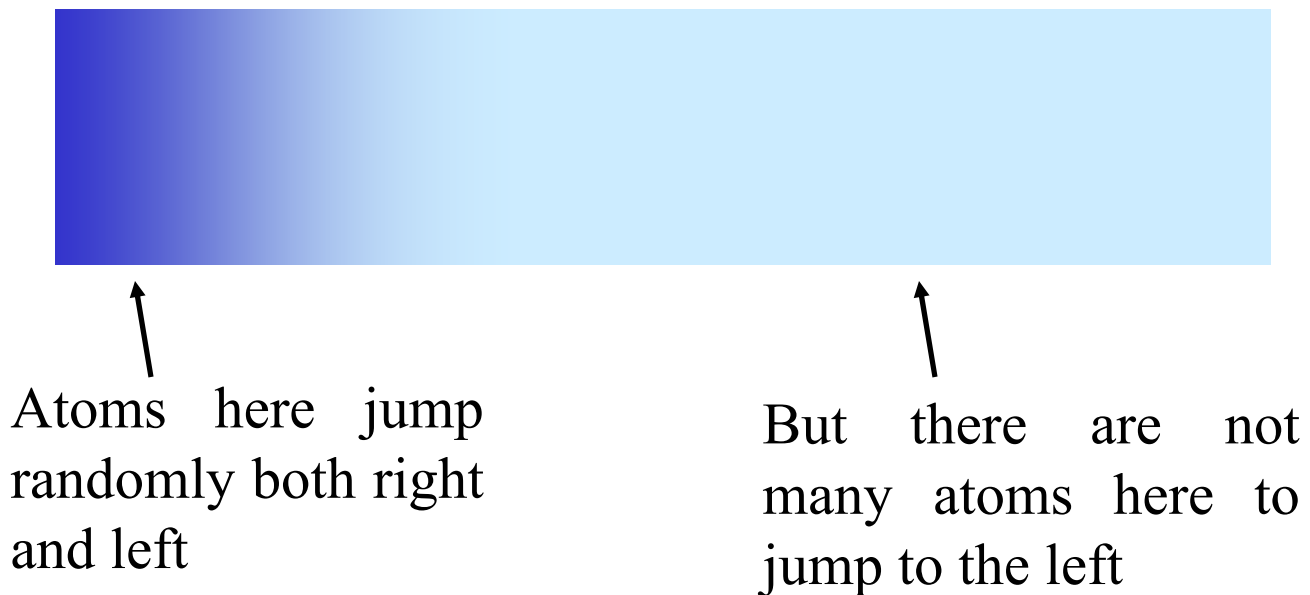
Diffusion against the concentration gradient

Spinodal decomposition vs. nucleation and growth

## Driving force for diffusion

In general, it is common for atoms to diffuse from regions of high concentration towards the regions of low concentration. Thus, the phenomenological Fick's laws describe the diffusion in terms of the relationships between the diffusion flux and concentration gradient.

E.g., consider ideal solution:



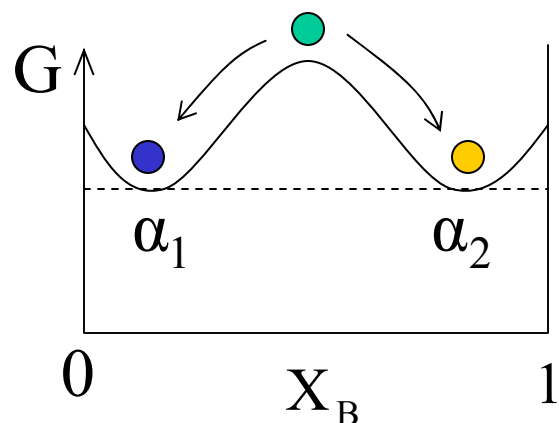
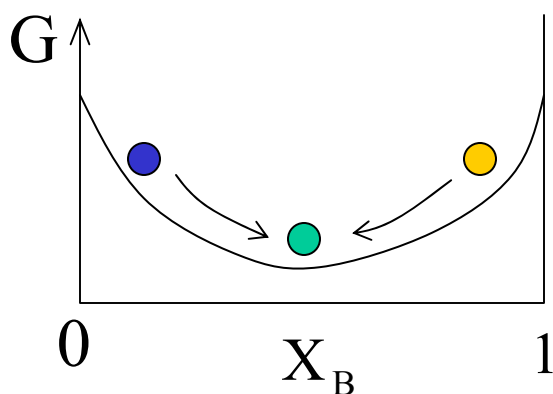
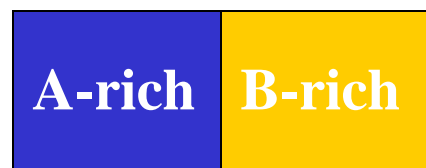
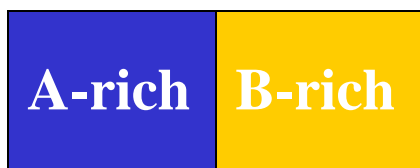
As a result there is a net flux of atoms from left to right.

The thermodynamic properties of solid solutions, however, play an important role in diffusion and, under certain conditions, may even induce the diffusion against the concentration gradient ( $D < 0$ )!

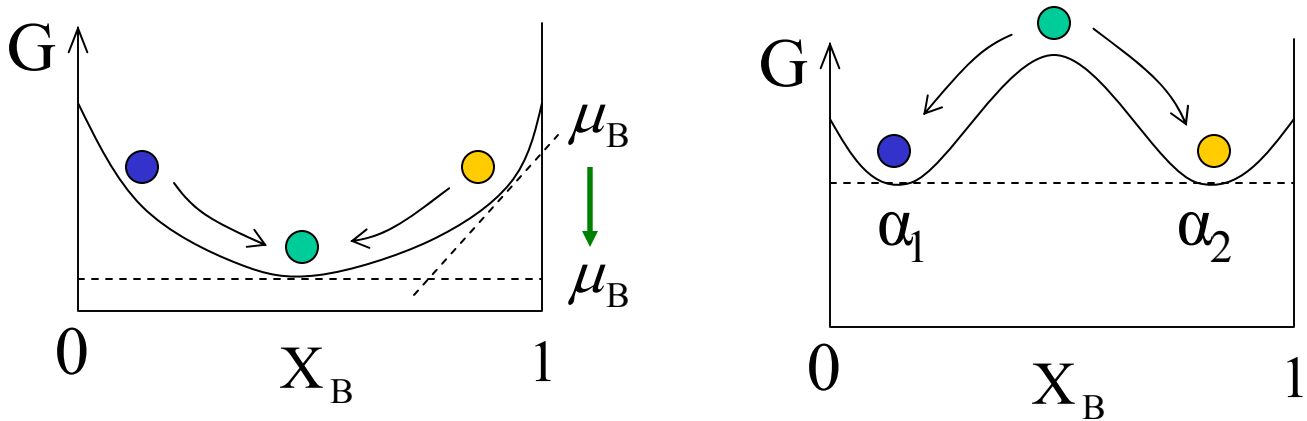
## Driving force for diffusion (I)

The *empirical* Fick's first law assumes proportionality between the diffusion flux and the concentration gradient. But thermodynamics tells us that any spontaneous process should go in the direction of **minimization of the free energy**.

As we can see from the examples below, atoms can diffuse from regions of high concentration towards the regions of low concentration – down the concentration gradient (left) as well as from the regions of low concentration towards the regions of high concentration – **up the concentration gradient?** (right)



## Driving force for diffusion (II)



Diffusion occurs so that the free energy is minimized and is therefore driven by the gradient of free energy.

The chemical potential of atoms of type A can be defined as the free energy per mole of A atoms.  $G = \mu_A X_A + \mu_B X_B$

Therefore, the free energy gradient can be expressed through the chemical potential gradient:

$$J_x = -M_A C_A \frac{\partial \mu_A}{\partial X} \quad \text{where } M_A \text{ is the atomic mobility of A atoms.}$$

In both cases the A and B atoms are diffusing from the regions where chemical potential is high to the regions where chemical potential is lower. **The driving force for diffusion is gradient of chemical potential.**

Atoms migrate so as to remove differences in chemical potential. Diffusion ceases at equilibrium, when

$$\mu_B^{\alpha_1} = \mu_B^{\alpha_2} \quad \text{and} \quad \mu_A^{\alpha_1} = \mu_A^{\alpha_2}$$

## Driving force for diffusion (III)

Chemical potential gradient is the driving force for diffusion:

$$J_x = -M_B C_B \frac{\partial \mu_B}{\partial X} \quad \text{where } M_B \text{ is mobility of B atoms}$$

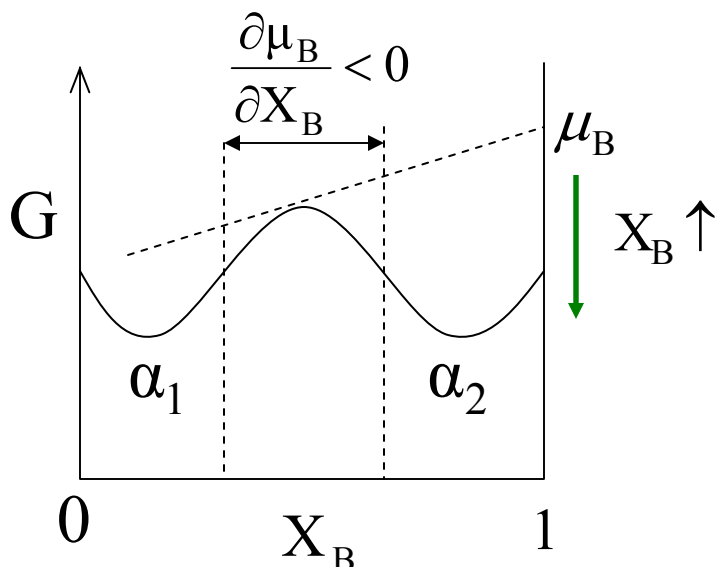
$$J_x = -D_B \frac{\partial C_B}{\partial X} \implies D_B = M_B C_B \frac{\partial \mu_B}{\partial C_B} = M_B X_B \frac{\partial \mu_B}{\partial X_B}$$

if  $\frac{\partial \mu_B}{\partial X_B} > 0$ , then  $D_B > 0$  - gradient of chemical potential is in the same direction as the concentration gradient.

if  $\frac{\partial \mu_B}{\partial X_B} < 0$ , then  $D_B < 0$  - diffusion occurs against the concentration gradient!

For example, we can identify regions with negative  $\partial \mu / \partial X_B$  in a system with miscibility gap:

We will discuss the behavior of homogeneous solution cooled within the miscibility gap later, after deriving equations for diffusion flux in ideal and regular solutions.



## Driving force for diffusion (IV)

Lets consider diffusion driven by the chemical potential gradient for ideal and regular solutions.

$$J_x = -M_B C_B \frac{\partial \mu_B}{\partial x}$$

**For an ideal solution:**  $\mu_B = G_B + RT \ln X_B$

$$\frac{\partial \mu_B}{\partial x} = \frac{\partial \mu_B}{\partial X_B} \frac{\partial X_B}{\partial x} = \frac{RT}{X_B} \frac{\partial X_B}{\partial x} = \frac{RT}{C_B} \frac{\partial C_B}{\partial x}$$

$$J_B = -M_B RT \frac{\partial C_B}{\partial x} = -D_B \frac{\partial C_B}{\partial x} \quad D_B = M_B RT$$

**For a regular solution:**  $\mu_B = G_B + \Omega(1 - X_B)^2 + RT \ln X_B$

$$\frac{\partial \mu_B}{\partial x} = \frac{\partial \mu_B}{\partial X_B} \frac{\partial X_B}{\partial x} = \frac{RT}{X_B} \left( 1 - \frac{2\Omega(1 - X_B)X_B}{RT} \right) \frac{\partial X_B}{\partial x} =$$

$$= \frac{RT}{C_B} \left( 1 - \frac{2\Omega X_A X_B}{RT} \right) \frac{\partial C_B}{\partial x} \quad D_B = M_B RT F$$

F

The factor in brackets is termed *the thermodynamic factor F*. It defines how inter-atomic interaction affects the diffusion of the atoms in the presence of concentration gradient.

## Driving force for diffusion (V)

As shown below, the thermodynamic factor is the same for both species A and B at a given composition and *is related to the curvature of the free energy curve*.

$$G^{\text{reg}} = X_A G_A + X_B G_B + \Omega X_A X_B + RT[X_A \ln X_A + X_B \ln X_B]$$
$$= (1 - X_B)G_A + X_B G_B + \Omega(1 - X_B)X_B + RT[(1 - X_B)\ln(1 - X_B) + X_B \ln X_B]$$

$$\frac{\partial G}{\partial X_B} = -G_A + G_B + \Omega - 2\Omega X_B + RT\left[-\ln(1 - X_B) - \frac{(1 - X_B)}{(1 - X_B)} + \ln X_B + \frac{X_B}{X_B}\right] =$$

$$= -G_A + G_B + \Omega - 2\Omega X_B + RT[-\ln(1 - X_B) + \ln X_B] =$$

$$= G_B - G_A + \Omega(1 - 2X_B) + RT \ln\left(\frac{X_B}{1 - X_B}\right)$$

$$\frac{\partial^2 G}{\partial X_B^2} = -2\Omega + RT\left[\frac{1}{1 - X_B} + \frac{1}{X_B}\right] = -2\Omega + \frac{RT}{X_A X_B}$$

$$\frac{\partial \mu_B}{\partial X} = \frac{RT}{C_B} \left(1 - \frac{2\Omega X_A X_B}{RT}\right) \frac{\partial C_B}{\partial X} = \frac{RT}{C_B} F \frac{\partial C_B}{\partial X}$$

$$F = \left(1 - \frac{2\Omega X_A X_B}{RT}\right) = \frac{X_A X_B}{RT} \frac{\partial^2 G}{\partial X_B^2}$$

## Driving force for diffusion (VI)

The presence of a strain energy gradient, an electric field, or a temperature gradient can also affect the diffusion and, in particular, can induce diffusion of atoms against the concentration gradient.

For example, in the presence of a strain energy gradient the equation for the chemical potential will include an elastic strain energy term  $E(x)$ . For a regular solution we have

$$\mu_B = G_B + \Omega(1 - X_B)^2 + RT \ln X_B + E$$

$$\frac{\partial \mu_B}{\partial x} = \frac{RT}{C_B} F \frac{\partial C_B}{\partial x} + \frac{\partial E}{\partial x}$$

$$J_B = -M_B C_B \frac{\partial \mu_B}{\partial x} = -M_B RT F \frac{\partial C_B}{\partial x} - M_B C_B \frac{\partial E}{\partial x}$$

$$J_B = -D_B \frac{\partial C_B}{\partial x} - \frac{D_B C_B}{RT F} \frac{\partial E}{\partial x} \quad D_B = M_B RT F$$



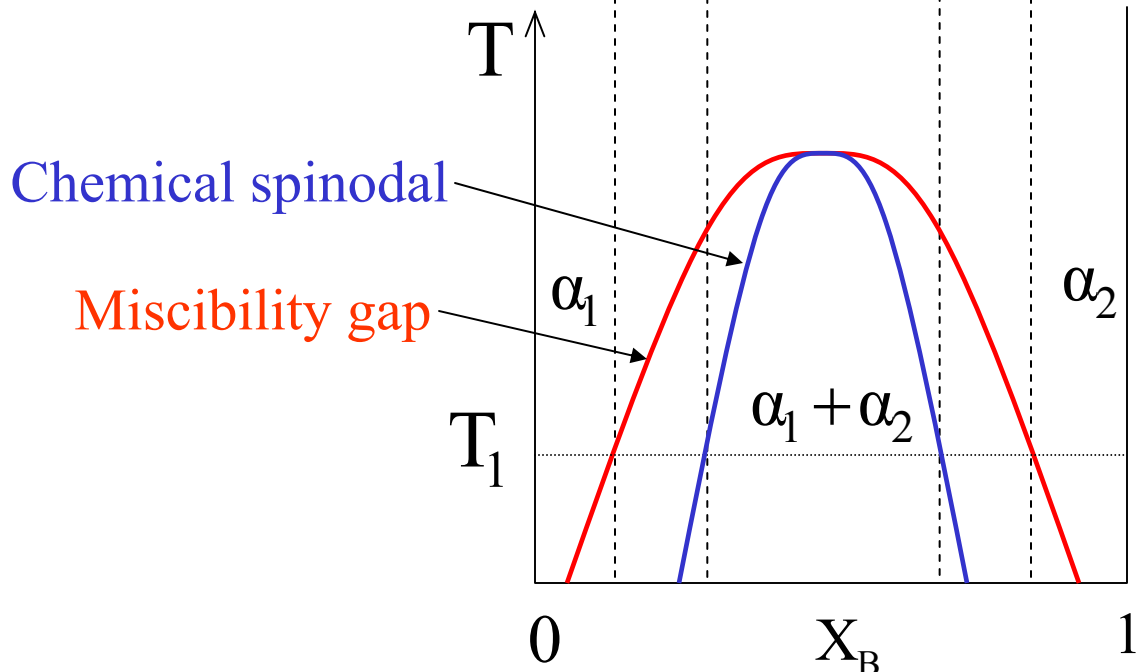
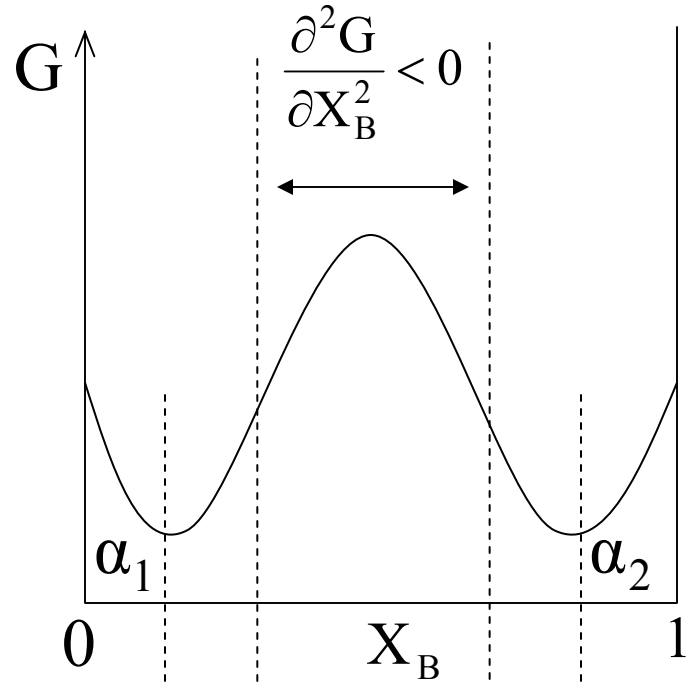
## Diffusion against the concentration gradient: Spinodal Decomposition

When the free energy curvature is negative, the thermodynamic factor  $F$  is negative, and the diffusion is directed against the concentration gradient:

$$\frac{\partial^2 G}{\partial X_B^2} < 0 \implies F < 0$$

$$D_B = M_B R T F < 0$$

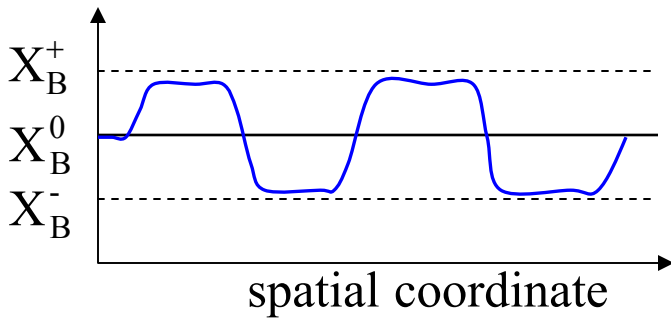
$$J_B = -D_B \frac{\partial C_B}{\partial X}$$



## Spinodal Decomposition

Homogeneous solution cooled into the miscibility gap will decompose into  $\alpha_1$  and  $\alpha_2$  so that the total free energy of the system decreases.

The mechanism of decomposition into  $\alpha_1$  and  $\alpha_2$  is different within the chemical spinodal region and outside (in the nucleation regions). Let's consider small fluctuations around the average composition  $X_B^0$ :



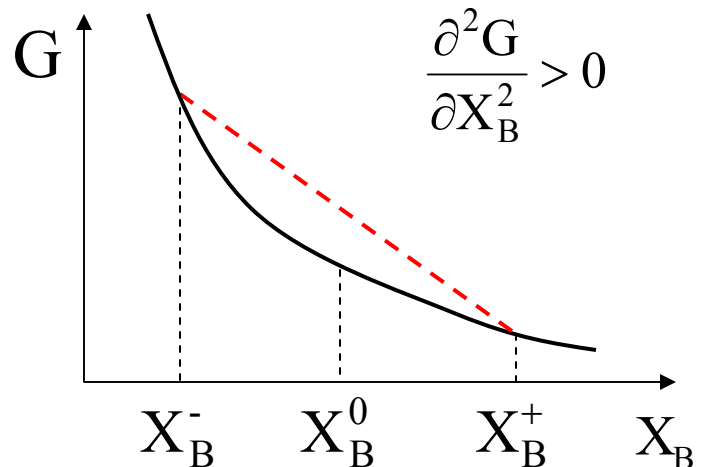
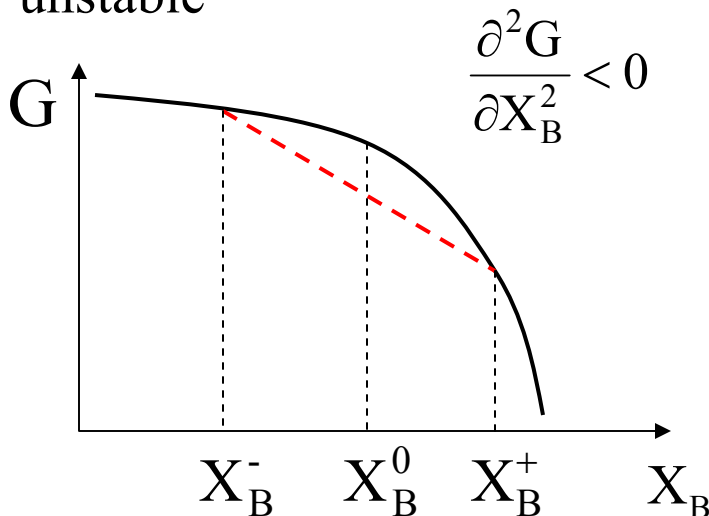
$$X_B^+ \ll \alpha_2 \quad X_B^+ \approx X_B^- \approx X_B^0$$

(fluctuations are small)

$$X_B^- \gg \alpha_1$$

Free energy decreases as a result of an arbitrary infinitesimal fluctuation in composition – the system is unstable

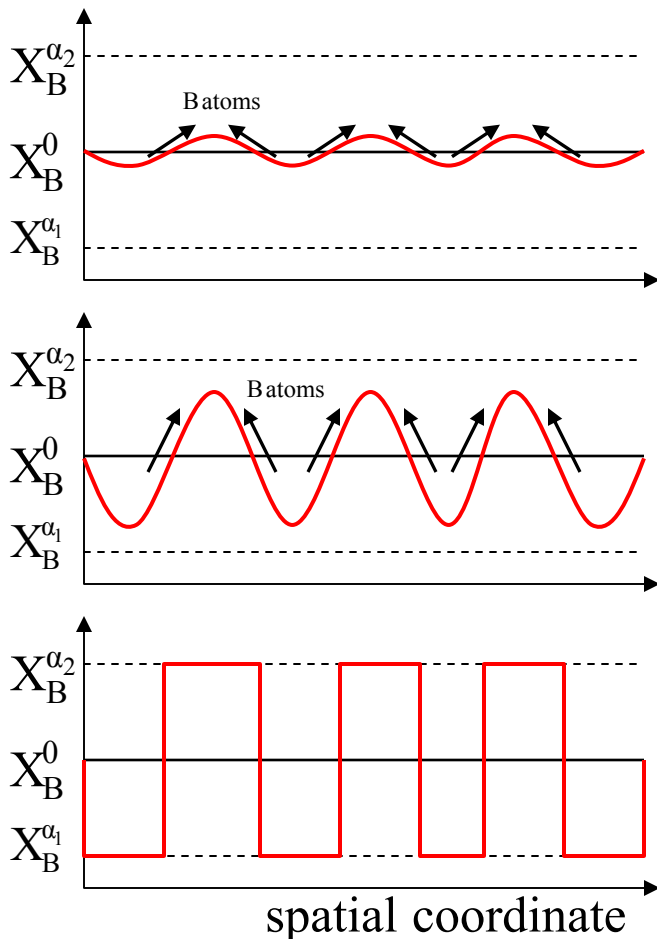
Free energy increases as a result of an infinitesimal fluctuation in composition – the system is stable with respect to small fluctuations



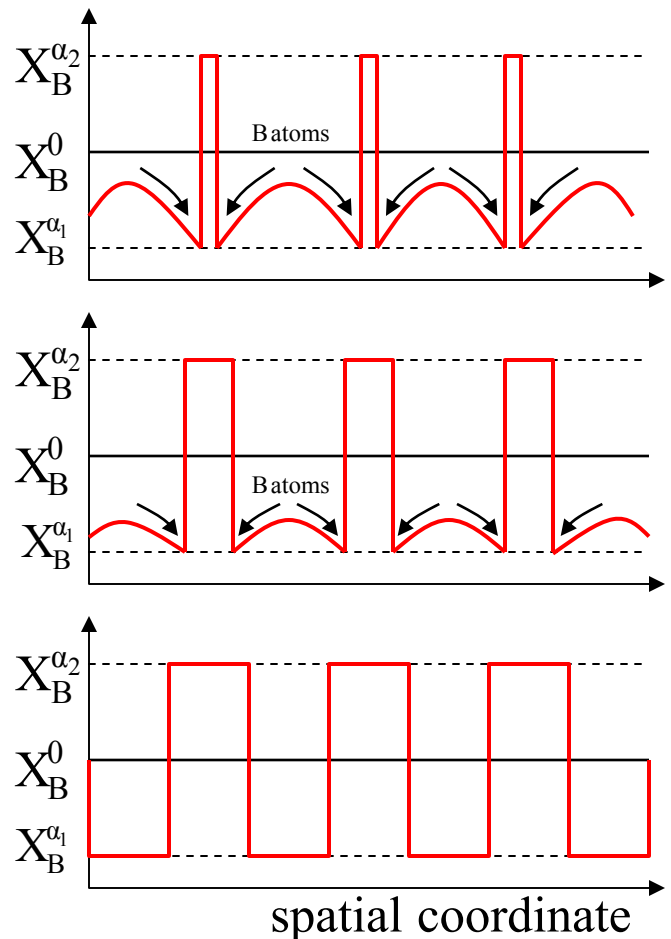
# Spinodal Decomposition

Although the system within the miscibility gap but outside the spinodal region is stable (metastable) with respect to small fluctuations, it is unstable to the separation into  $\alpha_1$  and  $\alpha_2$  determined by the common tangent construction. There is large difference in composition between  $\alpha_1$  and  $\alpha_2$  and large composition fluctuations are required in order to decrease the free energy. A process of formation of a large composition fluctuation is called **nucleation**. The phase separation is occurring in this case by **nucleation and growth** (will be discussed later).

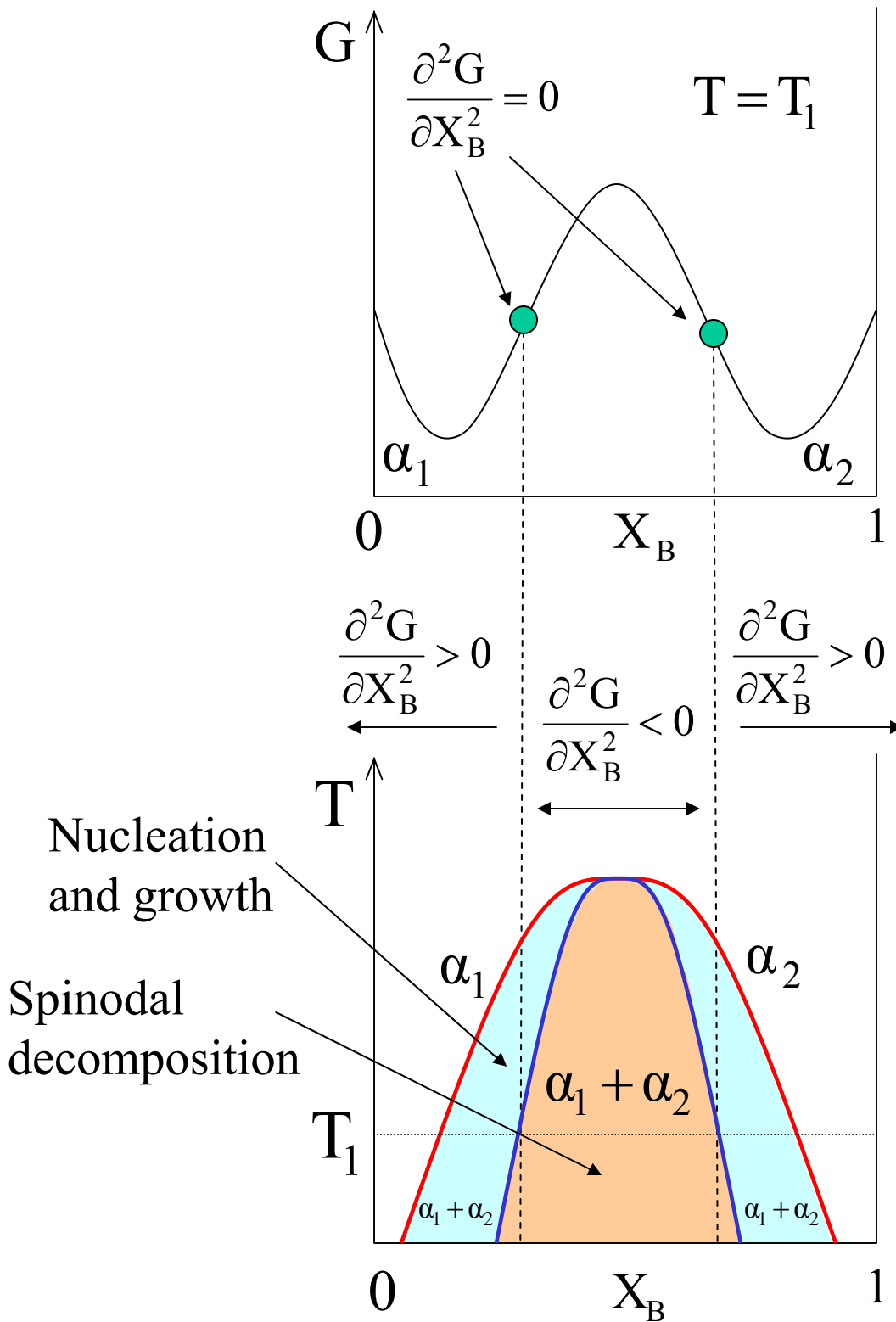
### Spinodal decomposition



### Nucleation and growth

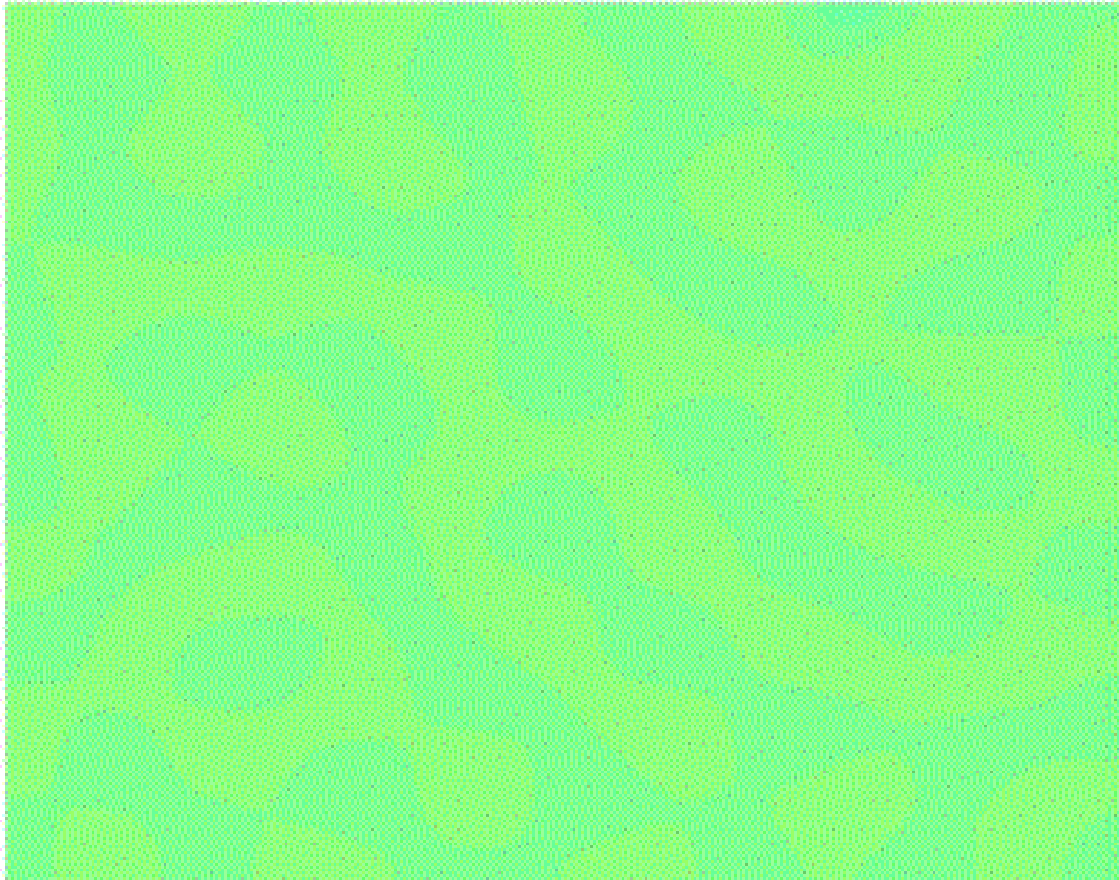


# Region of spinodal decomposition on a phase diagram with a miscibility gap



# Computer simulation of spinodal decomposition in a binary alloy

Time = 0.1 Epsilon = 0.02



<http://math.gmu.edu/~sander/movies/spinum.html>

## Computer simulation of laser overheating & explosive boiling

Short pulse laser irradiation leads to strong superheating and rapid decomposition of a surface region of the target into a mixture of gas phase atoms and liquid droplets

