

## Exsolution and Ordering in Solid Solutions

### 1.1 Introduction to solid solutions

A **solid solution** is a single phase which exists over a range of chemical compositions. Some materials are able to tolerate a wide and varied chemistry, whereas others permit only limited chemical deviation from their ideal chemical formulae. In many cases, the extent of solid solution is a strong function of temperature – with solid solution being favoured at high temperatures and phase separation (exsolution or precipitation) or ordering favoured at low temperatures.

For a multi-component material to exist as a single-phase solid solution, the components must be intimately mixed and (essentially) randomly distributed at the atomic scale, so that when the material is viewed at the nm- $\mu\text{m}$  length scales, it appears chemically homogeneous (Fig. 1).

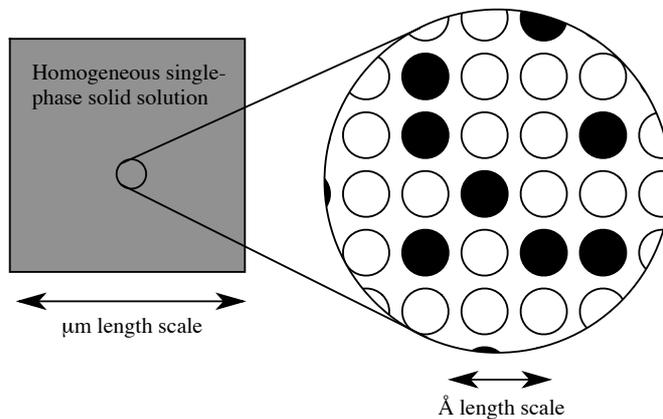


Fig. 1. When viewed at the atomic length scale, a solid solution is an intimate mixture of different chemical species, randomly distributed over the available crystallographic sites. When viewed at larger length scales, it appears as a homogeneous single phase with an average chemical composition.

In this practical we will explore the factors affecting the stability of solid solutions, and the different types of microstructure that are generated when solid solutions become unstable. The practical is in two parts. You should aim to spend 1 hour on each part.

### What you should know by the end of the practical!

- i. What is meant by the term ‘solid solution’, ‘exsolution’, and ‘ordering’
- ii. Understand the basic principle of a Monte Carlo simulation
- iii. Understand why a positive enthalpy of mixing leads to exsolution and why a negative enthalpy of mixing leads to ordering
- iv. Understand the origin of exsolution microstructures and antiphase domains

## 1.2 Liquid immiscibility and critical opalescence

In many materials, mixing components at the atomic scale is energetically unfavourable. At low temperatures, such materials exist as an intergrowth of two phases rather than a single-phase solid solution. The solid solution may become stable at higher temperatures, however, due to its higher entropy (this concept is explored in Section 2). This leads to a transition from a two-phase intergrowth to a single-phase solid solution at a critical temperature on heating. The locus of critical temperatures as a function of bulk composition is called the '*solvus*'. The solvus separates the stability field of the single-phase solid solution from the stability field of the two-phase intergrowth (the '*miscibility gap*').

The transition from two phases to a single phase (and vice-versa) can be demonstrated on a laboratory timescale using a mixture of two suitable liquids. Aniline and cyclohexane are immiscible over a wide range of compositions below about 28 °C, but become miscible on heating (Fig. 2).

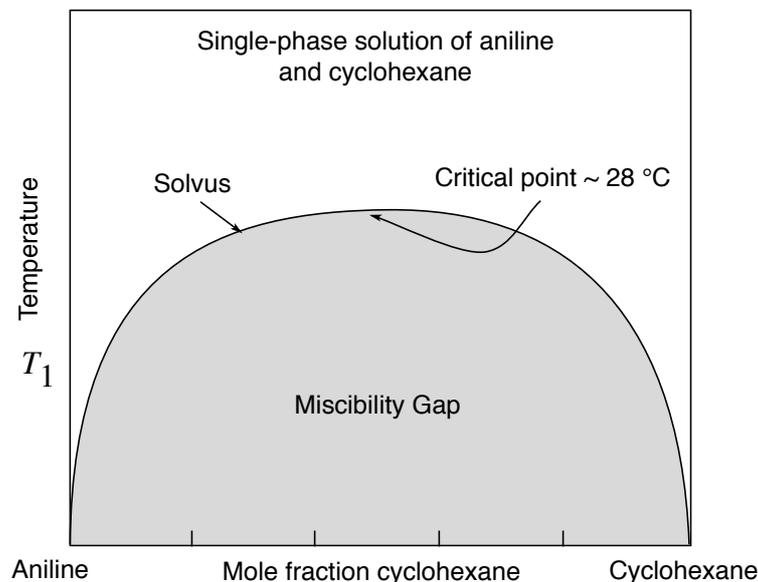


Fig. 2. Schematic equilibrium phase diagram for the binary system aniline-cyclohexane.

**WARNING: Both aniline and cyclohexane are highly flammable and carcinogenic. Be VERY careful not to break the sealed tubes.**

(a) You are provided with a sealed tube containing a 50:50 mixture of aniline and cyclohexane. Draw a sketch of the tube, noticing that, at room temperature, the two liquids are immiscible and are separated by a clear meniscus.

(b) Use the hairdryer to gently warm the sealed tube, while mixing the liquids by agitating the metal staples with a magnet. Describe what happens to the appearance of the two liquids as the tube slowly heats up. Be careful not to overheat the tubes (switch off the hairdryer as soon as the transition has taken place).

(c) Place a dot on Fig. 2 corresponding to the current approximate position of the system in temperature-composition space. What stability field is the system in at this temperature? Does this agree with your experimental observations?

### **Warning: Laser Light is Very Bright**

The He-Ne lasers you will be using are of comparatively low power, nominally 0.5 mW, and thus not particularly dangerous. The intensity of the light in the main laser beam is similar to sunlight, and thus the damage which it could inflict on the retina is closely equivalent to that which would result from forcing oneself to look directly into the sun. For this reason never look along the laser beam and be careful to prevent it from reaching anybody else in the laboratory.

(d) Switch off the hairdryer in order to let the sealed tube cool down, while still mixing. Place the black screen approximately 50 cm behind the sealed tube. Switch on the laser and aim the laser beam through the sealed tube and onto the screen (be careful not to blind any of your fellow students!).

Observe and describe what happens to the spot of laser light as the tube cools down. This may take several minutes. If you have time, you can make the same observations during heating.

**Explanation (you can read this in your own time if you wish)**

What you have just observed is the phenomenon of *critical opalescence*. Above the critical temperature, the system is a single-phase solution. On a length scale equivalent to the wavelength of the laser light (i.e. several hundred nm), the solution appears completely homogeneous. Hence the laser light passes straight through the material, yielding a sharp spot on the screen.

As the liquid approaches the critical temperature, its composition begins to fluctuate on a length scale similar to that of the wavelength of light. In other words, one region in the liquid will temporarily become enriched in aniline and depleted in cyclohexane, while a region several hundred nm away will become temporarily enriched in cyclohexane and depleted in aniline. The fluctuations in composition (which are approximately sinusoidal) cause fluctuations in the refractive index,  $n$ , of the solution. Light will scatter in proportion to the squared amplitude of the fluctuation in  $n$ . The sinusoidal fluctuations in refractive index act as diffraction gratings, scattering the light in different directions. Above the critical temperature, these fluctuations are unstable and continuously grow and decay away, leading to the dynamic ‘fluttering’ of the laser beam. Below the critical temperature, the fluctuations in composition become stable and grow in amplitude (since the system now wants to form separate aniline-rich and cyclohexane-rich phases). This leads to a rapid increase in scattering, causing the laser beam to become very diffuse very quickly. Eventually, the compositional fluctuations grow and coalesce to form discrete phases. The laser beam then returns to a single sharp spot.

A similar mechanism of phase separation via the growth of sinusoidal fluctuations in composition occurs in solids (Fig. 3). The process is referred to as *spinodal decomposition*, and it can provide an alternative to the nucleation and growth mechanism of phase separation under certain circumstances.

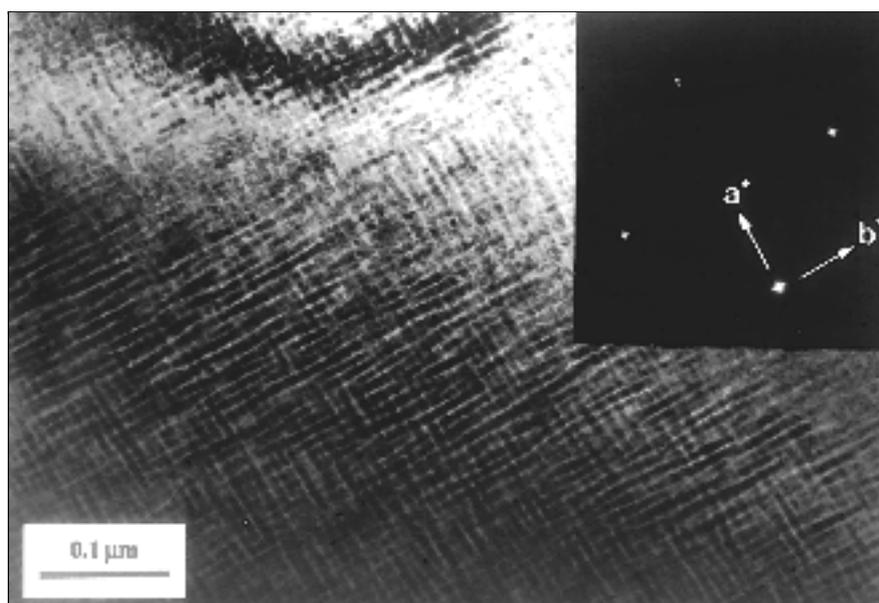


Fig. 3. Compositional fluctuations in the mineral  $\text{Fe}_3\text{O}_4\text{-MgAl}_2\text{O}_4$  due to spinodal decomposition

### 2.1 Computer simulation of cation ordering and exsolution

A good way to develop an understanding of solid solutions at the atomic scale is to perform a computer simulation. In this section we will describe a simple two-dimensional model of a solid solution, and then use a computer package to explore how the system behaves under a variety of different conditions.

The solid solution will consist of two components, A and B, distributed on a simple square lattice, as shown in Fig. 4.

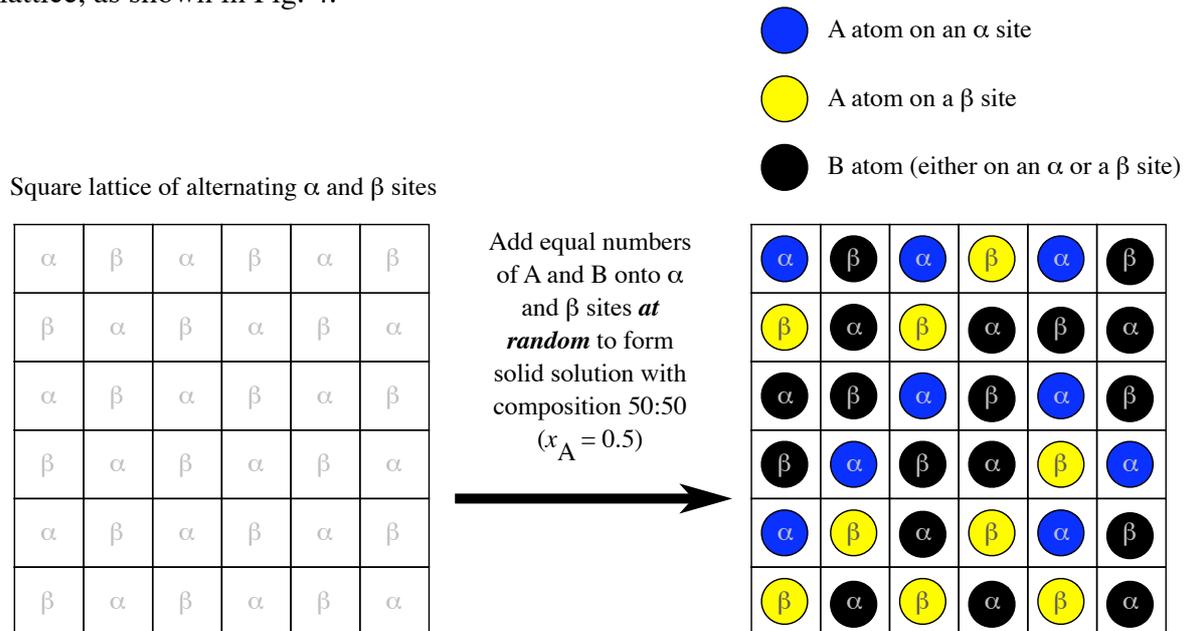


Fig. 4. Square lattice and colour coding of atoms in the model

The square lattice can be considered as a chess board, with alternating squares labelled  $\alpha$  and  $\beta$  for reference. Onto each square we can place an A or a B atom. If atoms are placed at random we form a solid solution with bulk composition:

$$x_A = N_A / (N_A + N_B)$$

where  $N_A$  and  $N_B$  are the numbers of A and B atoms, respectively (total number of atoms  $N = N_A + N_B$ ). The atoms are colour coded according to which site they sit on (for reasons that will become apparent later). An A atom sitting on an  $\alpha$  site is blue, an A atom sitting on a  $\beta$  site is yellow, and B atoms are black, irrespective of which site they are on.

There are three types of nearest neighbour bonds (A-A, B-B, and A-B), each associated with a particular ‘bond energy’ ( $W_{AA}$ ,  $W_{BB}$ , and  $W_{AB}$ ). The total energy of the system is then:

$$E = N_{AA}W_{AA} + N_{BB}W_{BB} + N_{AB}W_{AB}$$

where  $N_{AA}$ ,  $N_{BB}$ , and  $N_{AB}$  are the numbers of A-A, B-B, and A-B nearest-neighbour bonds in the system.

This energy can be rewritten in terms of just the number of A-A nearest neighbour bonds (see appendix for derivation):

$$E = E_0 - J N_{AA}$$

where  $E_0$  is a constant and  $J = (2W_{AB} - W_{AA} - W_{BB})$ .

The relative energy of any configuration of A and B atoms can now be calculated by simply counting the number of A-A nearest neighbours and multiplying by  $J$ .  $J$  is called the **interaction parameter** for each pair, and is determined by the energy of an A-B bond relative to the average energy of an A-A and a B-B bond (remember, a strong bond has a large negative value of  $W$ ).

A **positive** value of  $J$  means that A-A bonds are energetically **favourable**, and the system will attempt to **maximise** the number of A-A nearest neighbours.

A **negative** value of  $J$  means that A-A bonds are energetically **unfavourable**. The system will attempt to **avoid** A-A nearest neighbours.

## 2.2 Monte Carlo simulation with positive $J$ (exsolution)

The principle of a Monte Carlo simulation is shown as a flow chart in Fig. 5. Two atoms are chosen at random and their positions are swapped. The change in energy of the system  $\Delta E$  is calculated by counting the change in the number of A-A bonds before and after the swap and multiplying by  $J$ . If  $\Delta E$  is negative then the swap is accepted. If  $\Delta E$  is positive, then the swap is accepted with a probability  $\exp(-\Delta E/RT)$  (the Boltzmann probability). This means that energetically unfavourable swaps are much more likely to be accepted at high temperatures than at low temperatures. The process is then repeated many thousands of times, until the system approaches equilibrium.

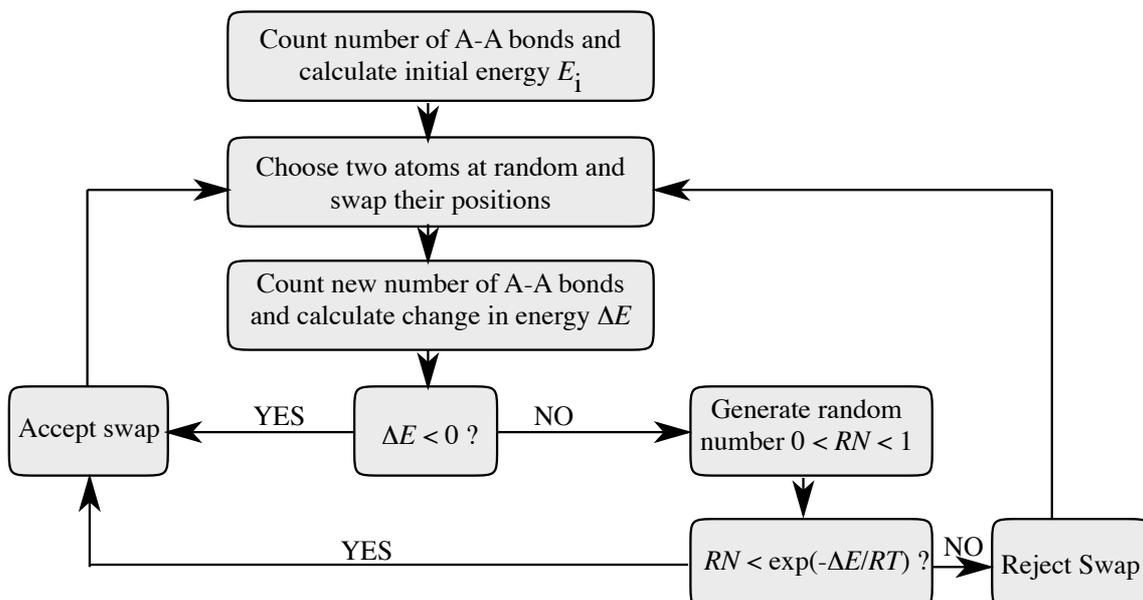


Fig. 5. Flow chart for a Monte Carlo simulation

(a) On the computer, double click the file “2D Monte Carlo” located on the desktop. You are presented with three windows entitled “2D Monte Carlo”, “Control Panel”, and “Simulation”. The first window can be ignored (you can minimise it to the task bar (windows) or dock (mac) by clicking the middle window widget).

The “Simulation” window shows a 2-dimensional square lattice of 100x100 sites. Each site is occupied by an A or a B atom (see Fig. 4 for colour coding).

The “Control Panel” window allows us to control the main parameters of the simulation: “Interaction parameter” controls the value of  $J$  (in units of J/mol), “Composition” controls the value of  $x_A$ , and “Temperature” controls the temperature at which the simulation will be run (in Kelvin)

(b) Set  $J = 5000$  J/mol,  $x_A = 0.5$ , and  $T = 1000$  K. Click on the button “Initialise Disordered”. This generates a random distribution of A and B atoms (in equal proportions). Note that the solid solution appears quite heterogeneous when viewed at the unit-cell scale, but that when viewed from a distance, the A and B atoms appear to be homogeneously distributed.

(c) Click the “Start MC Simulation” button to begin the simulation. The program performs 5000 Monte Carlo steps before the “Simulation” window is updated. A total of 50 sets of 5000 steps are performed before the simulation stops. You can stop the simulation at any time by pressing  $\text{⌘}+$ . (mac) or  $\text{ctrl}+\text{break}$  (windows).

Note the presence of small A-rich and B-rich clusters several unit cells thick, which come and go as the simulation proceeds. Averaged over time, however, the distribution of A and B atoms is essentially random.

(d) Stop the simulation and set the temperature to  $T = 600$  K. Restart the simulation by pressing the “Start MC Simulation” button. Note how the A-rich and B-rich clusters are more pronounced. Averaged over time, however, the distribution of A and B is still random.

(e) Gradually reduce the temperature in steps of 100 K. Describe qualitatively how the number of A-A, B-B, and A-B bonds changes as a function of temperature. What effect will these changes have on the enthalpy of the system?

(f) Compare the microstructure obtained at low temperatures with the microstructure observed when a real material exsolves (e.g. the Fe-Ni meteorite seen in the last practical). Can you account for the difference?

You should find that below a critical temperature, the A-rich and B-rich clusters become stable and grow into distinct A-rich and B-rich phases. The system has now transformed from a homogeneous single-phase solid solution into an intergrowth of two phases. By exsolving in this way, the system maximises the number of energetically favourable A-A and B-B bonds and minimises the number of energetically unfavourable A-B bonds.

### 2.3 Monte Carlo Simulation with negative $J$ (ordering)

With a negative  $J$ , the system will attempt to minimise the number of unfavourable A-A and B-B bonds and maximise the number of favourable A-B bonds. It can do this by **ordering** the atoms in such a way that A atoms are always surrounded by B atoms (and vice versa).

(a) Click on the button “Initialise Ordered”. This generates a perfectly ordered arrangement, with A atoms on  $\alpha$  sites (blue) and B atoms on  $\beta$  sites (black). How does the unit cell of the ordered structure compare with that of the disordered solid solution?

(b) Click on the button “Initialise Antiorordered”. How does this structure compare with that of the ordered structure? How many unfavourable A-A or B-B bonds are there in the ordered and antiorordered structures? How, therefore, do the enthalpies of the ordered and antiorordered structures compare?

(c) Set  $J = -5000$  J/mol,  $x_A = 0.5$ , and  $T = 300$  K. Click on the button “Initialise Ordered” and then start the simulation. Describe what happens to the number of A-A and B-B bonds in the system.

(d) Increase the temperature in steps of 100 K up to 600 K. Describe what happens to the degree of cation order in the system as a function of temperature. Can you identify a critical temperature at which the degree of long-range order breaks down? Compare the results of a simulation at  $T > 600$  K with a perfectly random configuration of A and B atoms. Can you identify any short-range order in the system?

On increasing temperature you should observe a transition from the initial ordered state, with all A atoms on  $\alpha$  sites (i.e. all A atoms coloured blue) to a disordered state with A atoms evenly distributed over  $\alpha$  and  $\beta$  sites (i.e. equal numbers of blue and yellow A atoms). This order-disorder phase transition occurs at a critical temperature (just as in the case of exsolution) although the precise temperature may be difficult to identify. Note that significant short-range order persists well above the critical temperature.

(e) Click on the “Initialise Disordered” button. Set the temperature to 100 K and start the simulation. This simulates the effect of taking a disordered material and cooling it rapidly through the critical temperature. Make a sketch of the resulting microstructure.

When a disordered material is quenched in this way, there is equal probability of forming either the ordered state (blue and black) or the equivalent antioderred state (yellow and black). This results in the formation of *antiphase domains*, separated by *antiphase boundaries*. The ordered and antioderred domains are exactly equivalent to each other, except that the A and B atoms are interchanged. The antiphase boundaries are a type of planar defect, and can be seen using electron microscopy (Fig. 6).

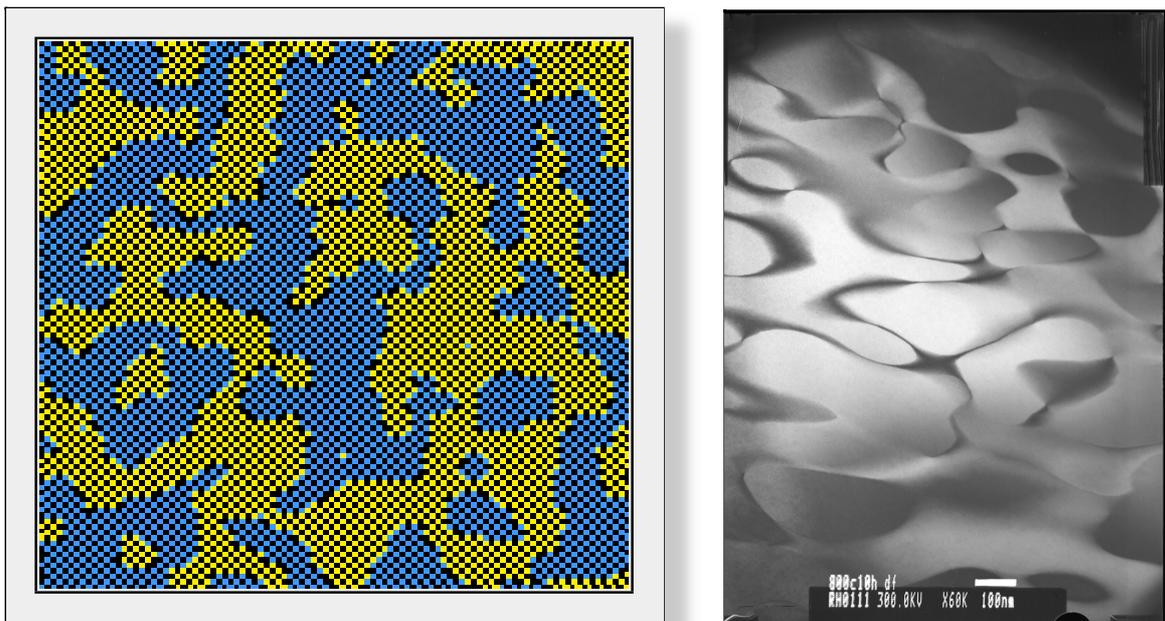


Fig. 6. Comparison of antiphase domains created in the simulation with those observed experimentally in the system  $\text{Fe}_2\text{O}_3\text{-FeTiO}_3$  using TEM.

(f) Set the composition of the solid solution to  $x_A = 0.4$  and click on the “Initialise Disordered” button. This generates a solid solution with the ratio of A:B atoms equal to 40:60. Set the temperature to 100 K and start the simulation. Look carefully at the antiphase boundaries generated. How do they differ from those obtained at the 50:50 composition? Can you explain this observation?

**APPENDIX (Read in your own time)****Energy of a general configuration of A and B atoms**

The total energy of any configuration of A and B atoms is:

$$E = N_{AA} W_{AA} + N_{BB} W_{BB} + N_{AB} W_{AB}$$

where  $N_{AA}$ ,  $N_{BB}$ , and  $N_{AB}$  are the numbers of A-A, B-B, and A-B nearest-neighbour bonds in the system and  $W_{AA}$ ,  $W_{BB}$ , and  $W_{AB}$  are the energies associated with each type of bond.

If the probability of an A atom sitting next to another A atom is  $P_{AA}$ , then:

$$N_{AA} = 1/2 z N x_A P_{AA}$$

where  $z$  is the coordination number of the lattice ( $z = 4$  in this case, as each atom is surrounded by 4 nearest neighbours),  $N$  is the total number of atoms,  $x_A$  is the mole fraction of A atoms in the system, and the factor of 1/2 is required to avoid counting each bond twice.  $N_{AB}$  and  $N_{BB}$  can now be written in terms of  $N_{AA}$ :

$$N_{AB} = z N x_A (1 - P_{AA}) = z N x_A - 2N_{AA}$$

$$N_{BB} = 1/2 z N - N_{AA} - N_{AB} = 1/2 z N (1 - 2x_A) + N_{AA}$$

Substituting these into the total energy equation and rearranging one finds:

$$E = z N x_A W_{AB} + 1/2 z N (1 - 2x_A) W_{BB} - (2W_{AB} - W_{AA} - W_{BB}) N_{AA}$$

For a fixed bulk composition, the first two terms remain constant as the distribution of A and B atoms changes, hence we can write:

$$E = E_0 - J N_{AA}$$

where  $E_0$  is a constant and  $J = (2W_{AB} - W_{AA} - W_{BB})$ .