

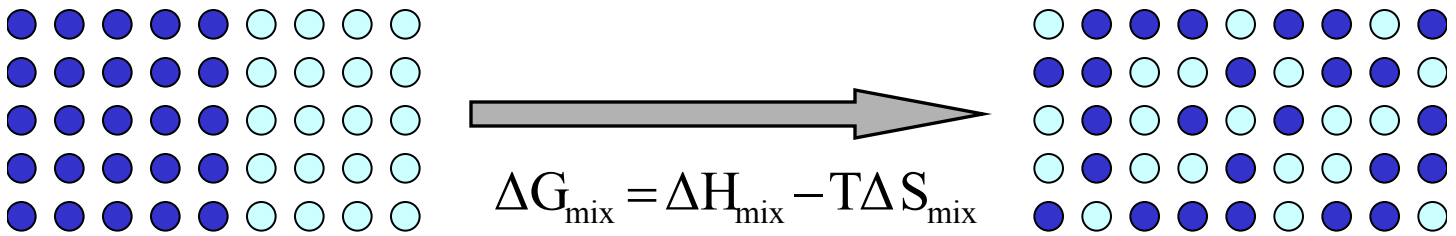
## Homework #4

**Objective:** Getting experience with Metropolis Monte Carlo simulations, using Ising model to study compositional ordering and segregation in binary alloys.

1. Review computer code that implements a simple Ising model, mse627-mc.f90, (the code was written recently and not thoroughly tested, if you find any bugs or get ideas for improvement please send them to the class mailing list).
2. Perform Metropolis Monte Carlo simulation (MC moves = switch particle types) to find equilibrium structure (and compositional ordering) for binary alloys with two sets of parameters ( $E_{AA} = E_{BB} = -0.05$  eV,  $E_{AB} = -0.01$  eV) and ( $E_{AA} = E_{BB} = -0.05$  eV,  $E_{AB} = -0.25$  eV) and several temperatures. Choose values of temperature that would allow you to discuss the temperature dependence of the results of the simulations.
3. Plot snapshots from your simulations to illustrate the structural changes during the simulations and the final equilibrium structures observed for different input parameters used (task #2). (*Snapshots can be made using the files written to sub-directory "data" – you should create this directory before running the code*). Make plots showing changes of energy, number of AA, AB, and BB bonds during the simulations. (*Plots can be made using the data written to file EnBnd.out*). **Discuss** your results based on thermodynamics of binary solid solutions briefly outlined in the next two pages.
4. Adapt the code to model a crystal with vacancies. Perform simulations for a system with energy of vacancy formation of 1 eV. Calculate the equilibrium vacancy concentrations for several (2-3) values of temperature. Compare your results to the theoretical equation derived/discussed below. **Discuss** agreement/disagreement between the numerical results and the theoretical equation.

## Brief (and somewhat oversimplified) introduction to basic thermodynamics of binary solutions

Let's consider mixing of two components A and B:



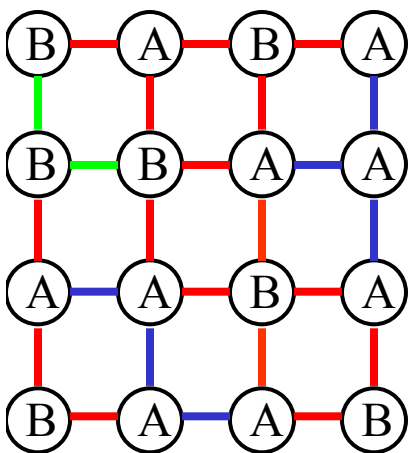
$\Delta G_{\text{mix}}$  is the change of the Gibbs free energy caused by the mixing.

$\Delta H_{\text{mix}}$  is the heat of mixing of the components (**heat of formation of a solution**)

$\Delta S_{\text{mix}}$  is the difference in entropy between mixed and unmixed states (**entropy of formation of a solution**)

$\Delta S_{\text{mix}}$  is always positive and reflects the increase in randomness of the atomic configuration (the number of ways the system can be rearranged for the same macroscopic state = “number of microstates”  $\Omega$ ) upon mixing.  $S = k_B \ln \Omega$

To analyze  $\Delta H_{\text{mix}}$  we can use a simple model called *statistical or quasi-chemical model*. In this model the heat of mixing (change in energy as we mix components, A and B) is only related to the bond energies between adjacent atoms. The assumptions are (1) random arrangement of atoms in the solution and (2) the interatomic distances and bond energies are independent of composition.



3 types of bonds:

A – A bond (energy  $E_{AA}$ )

A – B bond (energy  $E_{AB}$ )

B – B bond (energy  $E_{BB}$ )

The energy of mixing (heat of formation  $\Delta H_{\text{mix}}$ ) calculated within statistical or quasi-chemical model is

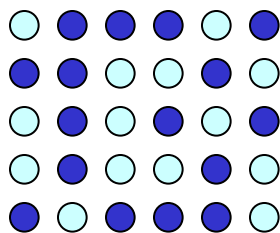
$$\Delta H_{\text{mix}} = P_{\text{AB}} \left( E_{\text{AB}} - \frac{E_{\text{AA}} + E_{\text{BB}}}{2} \right)$$

where  $P_{\text{AB}}$  is the number of bonds between atoms of type A and type B.

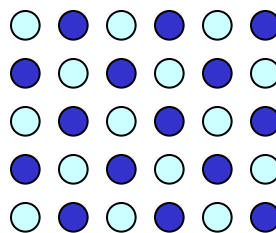
If  $E_{\text{AB}} = \frac{E_{\text{AA}} + E_{\text{BB}}}{2}$  the solution is ideal:  $\Delta H_{\text{mix}} = 0$

If  $E_{\text{AB}} > \frac{E_{\text{AA}} + E_{\text{BB}}}{2}$   $\Delta H_{\text{mix}} > 0$  – the internal energy is minimized by increasing the number of A-A and B-B bonds – can lead to clustering at low T

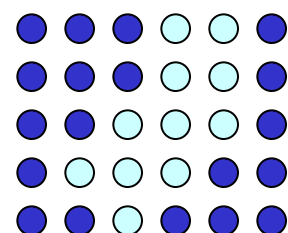
If  $E_{\text{AB}} < \frac{E_{\text{AA}} + E_{\text{BB}}}{2}$   $\Delta H_{\text{mix}} < 0$  – the internal energy is minimized by increasing the number of A-B bonds – can lead to ordered solution at low T



random



ordered



clustering

The arrangement of atoms is a result of compromise between the lowest internal energy and highest entropy. Degree of clustering or ordering decreases with increasing T since the entropy contribution ( $-TS$ ) to Gibbs free energy becomes more important.

More information can be found at

<http://www.people.virginia.edu/~lz2n/mse305/notes/BinarySolutions.pdf>

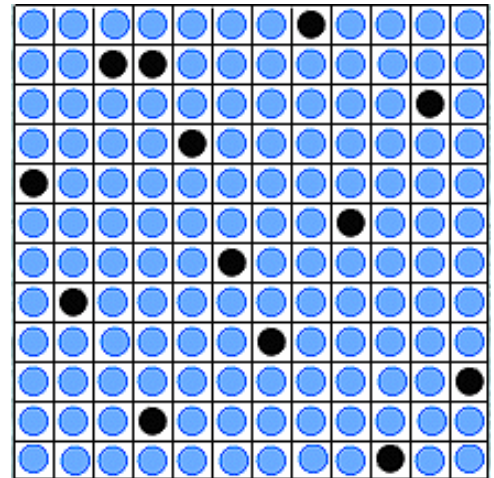
or any textbook on thermodynamics of materials

## Equilibrium vacancy concentration (from analysis of configurational entropy)

The configurational entropy of a crystal refers to the distinguishable ways the atoms can be arranged on the lattice sites. For monoatomic crystals the only origin of configurational entropy is the presence of crystal defects such as vacancies – lattice sites without atoms.

The removal of an atom from its lattice site

- breaks bonds and increases the internal energy of the material by  $\epsilon_v^f$ .
- Increases the randomness of the atomic configuration, and, thus,  $S_{\text{conf}}$ .



Let's first calculate the configurational entropy:

Consider a crystal lattice with  $N$  lattice sites and  $N-1$  atoms (one vacancy). Assume that  $N$  is large enough so that we can neglect the surface in our consideration and assume that all lattice sites are equivalent. In the system of  $N$  lattice sites we can have a vacancy in any of the  $N$  sites –  $N$  different configurations are possible and  $S_{\text{conf}}^1 = k_B \ln N$ .

If there are two vacancies, for each location of the first vacancy we have  $N-1$  locations of the second one. Therefore,

$S_{\text{conf}}^2 = k_B \ln [ \frac{1}{2} N (N-1) ] \gg S_{\text{conf}}^1$ . (  $\frac{1}{2}$  comes from the fact that vacancies are identical and the states where one vacancy is at the site  $i$  and the second one at  $j$ , are identical to the state  $(j,i)$  ).

$S_{\text{conf}}^3 = k_B \ln [ \frac{1}{6} N (N-1)(N-2) ] \gg S_{\text{conf}}^2, \dots$

## Equilibrium vacancy concentration (2)

The number of distinct configurations for  $n$  vacancies is

$$\frac{1}{n!} N(N-1)(N-2)\dots(N-n+1) = \frac{N!}{n!(N-n)!}$$

$$S_{\text{conf}}^n = k_B \ln \frac{N!}{n!(N-n)!}$$

The equilibrium concentration of vacancies is the one that corresponds to the minimum of free energy:  $A = U - TS$

Neglecting a small change in the thermal entropy due to the change in the vibrational frequencies of atoms around a vacancy (formation entropy), and ignoring the vacancy-vacancy interactions, we can write:

$$A^n = n\varepsilon_v^f - k_B T \ln \frac{N!}{n!(N-n)!}$$

If  $N$  is large enough, introduction of the first vacancy will reduce the free energy for any finite  $T$ :

$$A^1 = \varepsilon_v^f - k_B T \ln N < 0$$

The equilibrium concentration of vacancies can be found from:

$$\left. \frac{\partial A^n}{\partial n} \right|_{n=n_{\text{eq}}} = 0$$

### Equilibrium vacancy concentration (3)

Let's first consider  $\frac{\partial S_{\text{conf}}^n}{\partial n}$

using Stirling formula for big numbers:  $\ln N! \approx N \ln N - N$

$$\frac{\partial S_{\text{conf}}^n}{\partial n} = k_B \frac{\partial}{\partial n} \left\{ \ln \frac{N!}{n!(N-n)!} \right\} = k_B \frac{\partial}{\partial n} \{ \ln N! - \ln n! - \ln(N-n)! \} =$$

$$= k_B \frac{\partial}{\partial n} \{ N \ln N - N - n \ln n + n - (N-n) \ln(N-n) + (N-n) \} =$$

$$= k_B \frac{\partial}{\partial n} \{ N \ln N - n \ln n - (N-n) \ln(N-n) \} =$$

$$= k_B \left\{ -\ln n - 1 + \ln(N-n) - \frac{(N-n)}{(N-n)}(-1) \right\} = k_B \ln \left( \frac{N-n}{n} \right)$$

$$= -k_B \ln \left( \frac{n}{N-n} \right) \approx -k_B \ln \left( \frac{n}{N} \right)$$

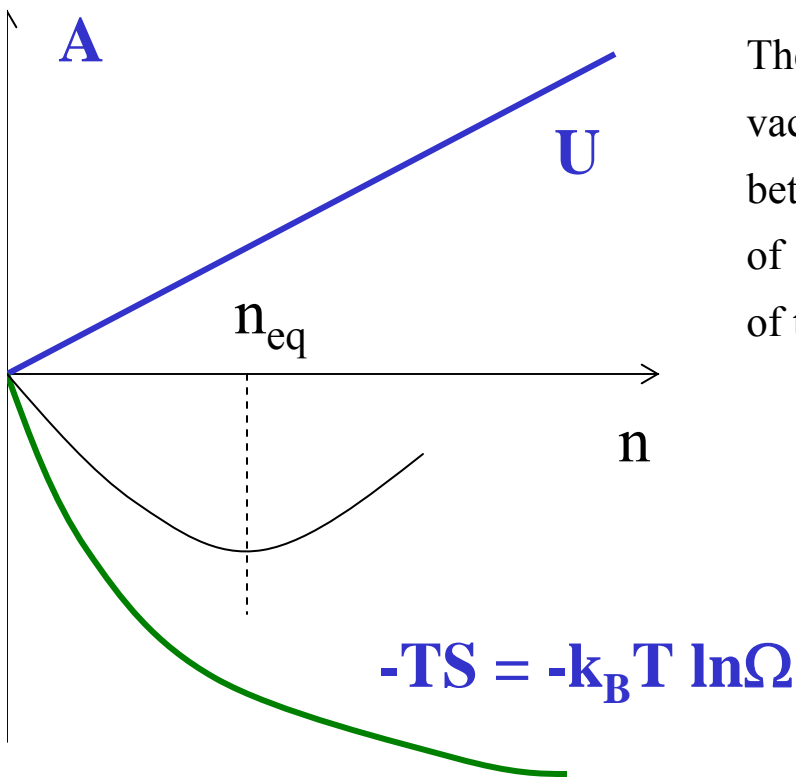
For the equilibrium concentration of vacancies:

$$\left. \frac{\partial A^n}{\partial n} \right|_{n=n_{\text{eq}}} = \left. \frac{\partial}{\partial n} \left\{ n \varepsilon_v^f - T S_{\text{conf}}^n \right\} \right|_{n=n_{\text{eq}}} = \varepsilon_v^f + k_B T \ln \left( \frac{n_{\text{eq}}}{N} \right) = 0$$

## Equilibrium vacancy concentration (4)

$$n_{\text{eq}} = N \exp\left(-\frac{\varepsilon_v^f}{k_B T}\right)$$

For metals,  $\varepsilon_v^f \approx 9k_B T_m$ . We can estimate that at room temperature in copper there is one vacancy per  $10^{15}$  lattice atoms, whereas just below the melting point there is one vacancy for every 10,000 atoms – very strong temperature dependence.



The equilibrium concentration of the vacancies is defined by the balance between the internal (potential) energy of vacancy formation and the increase of the configurational entropy.

The formation **energy**  $\varepsilon_v^f$  in crystals, that we used in the derivation, is practically indistinguishable from the formation **enthalpy**  $H_v^f$  which has to be used if the pressure and not the volume is kept constant.