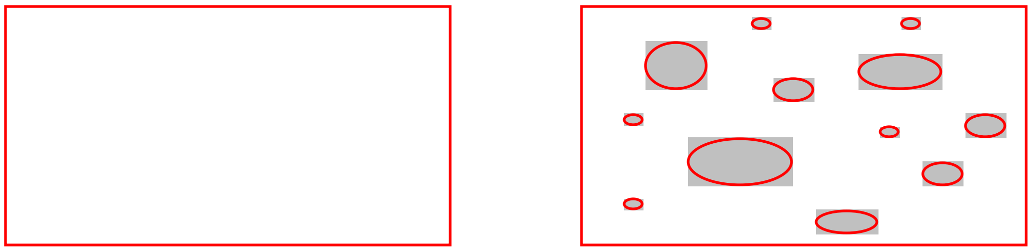
MIXING

- WILL A POLYMER DISSOLVE IN A GIVEN SOLVENT ?
- WILL A PARTICULAR POLYMER MIX WITH ANOTHER POLYMER ?

POLYMER SOLUTIONS AND BLENDS

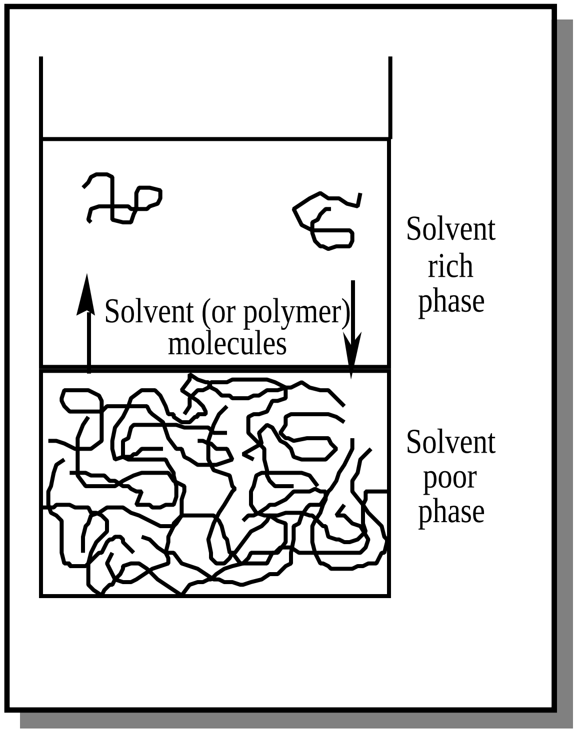
MISCIBLE **IMMISCIBLE**



Single phase **Phase separated**

← Blends

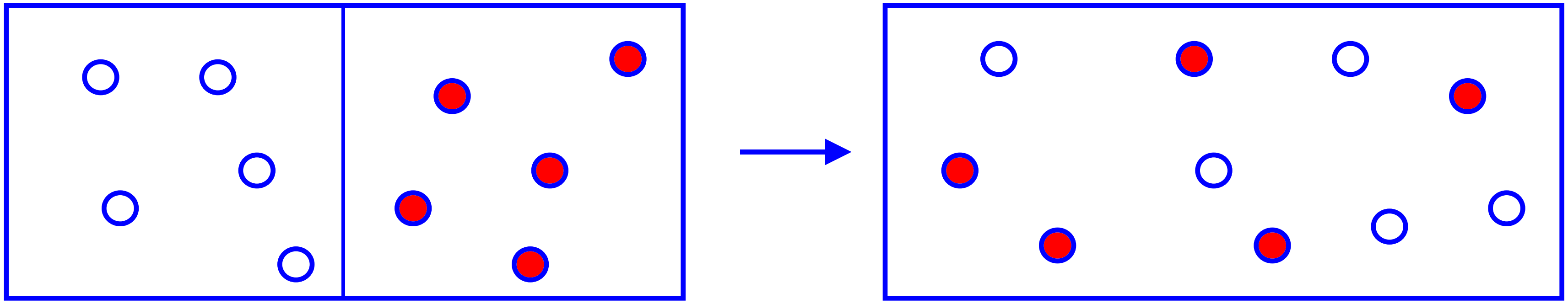
Phase separated solution →



CAN WE PREDICT PHASE BEHAVIOUR ?

THE SECOND LAW OF THERMODYNAMICS AND FREE ENERGY

For a process to occur spontaneously, S must increase; eg mixing



$$\Delta S_{tot} = \Delta S_{sys} + \Delta S_{surr}$$

But, if heat is released by the system

$$\Delta S_{surr} = -\frac{\Delta Q_{sys}}{T} = -\frac{\Delta H_{sys}}{T}$$

Define free energy

$$\Delta G = -T\Delta S_{tot} = \Delta H - T\Delta S$$

WHY BOTHER TO CALCULATE THE FREE ENERGY ?

1. **BECAUSE IF WE DON'T THE GHOSTS OF BOLTZMANN AND EHRENFEST WILL COME BACK TO HAUNT US**

2. **ONE CONDITION FOR FORMING A** SINGLE PHASE **IS THAT THE FREE ENERGY MUST BE NEGATIVE**

3. **THE OTHER CONDITION IS THAT THE** SECOND DERIVATIVE **OF THE FREE ENERGY MUST BE POSITIVE**

THEORIES OF MIXING

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

Assume the interactions between the molecules
Can be approximated by a mean field.This allows
The enthalpy and entropy to be treated seperately

BOLTZMANN’S TOMB

Entropy is associated with the distribution of energy and matter in a system.This can be expressed formally in terms of the equation carved on Boltzmann’s tomb

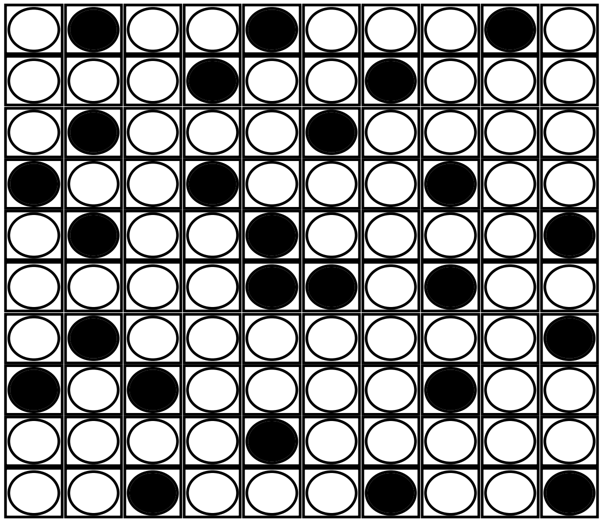
$$S = k \ln W$$

Which,today,is normally written

$$S = k \ln \Omega$$

Where Ω is the number of arrangements
Available to the system**[At a given V, E, N]**

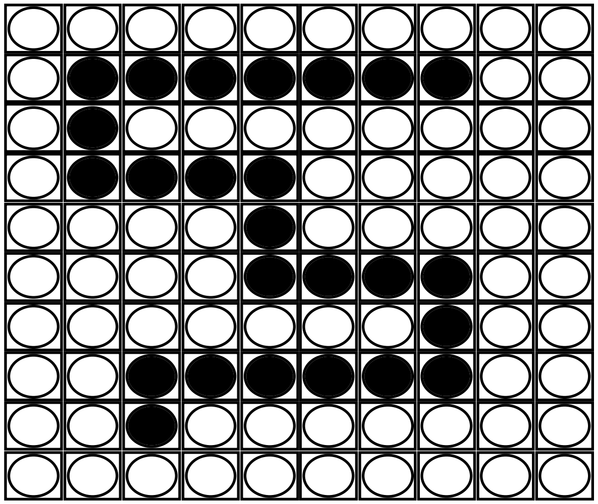
LATTICE MODELS - Summary



NUMBER OF CONFIGURATIONS

Equal-size small molecules

$$\frac{n_o!}{n_A!\, n_B!}$$



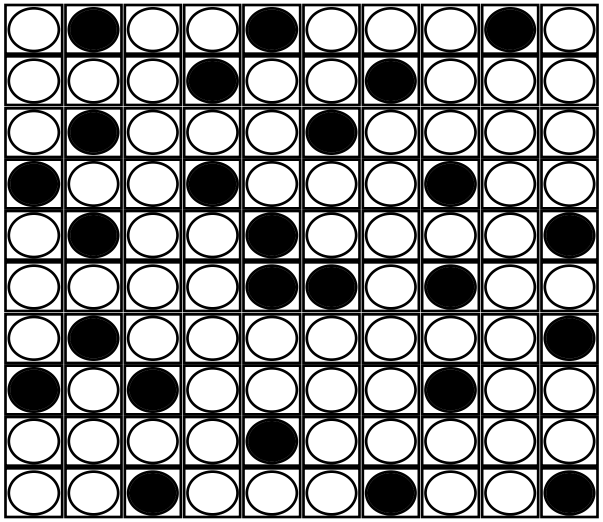
○ Solvent ● Polymer chain segment

Flory model for polymer solutions

$$\frac{n_o!}{n_A!\, N_B!}\left[\frac{(z-1)^{N_B(m-1)}}{\sigma^{N_B}}\;\frac{1}{n_o^{N_B(m-1)}}\right]$$

How are these expresions obtained ?

REGULAR SOLUTION THEORY



NUMBER OF CONFIGURATIONS

$$\Omega = \frac{\left[N_A + N_B\right]!}{N_A!\,N_B!}$$

HENCE

$$-\frac{\Delta S_m}{R} = n_A \ln x_A + n_B \ln x_B$$

SOME NOTES CONCERNING THE ENTROPY OF MIXING

THE QUANTITIES N_A OR N_B CAN EITHER BE THE NUMBER OF MOLECULES OF A AND B, RESPECTIVELY, OR THE NUMBER OF MOLES

THE CONSTANT CHANGES DEPENDING ON CHOICE

MOLES → R (or RT)
MOLECULES → k (or kT)

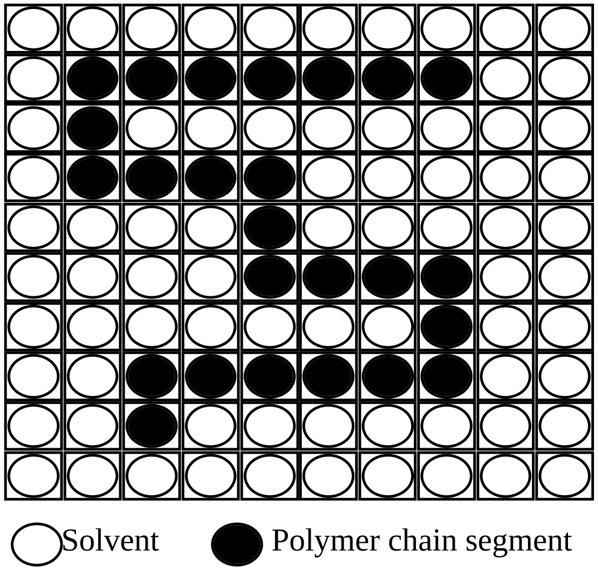
IN CALCULATING ΔS_m WE USED STIRLING'S APPROXIMATION

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

THE FINAL ANSWER IS WRITTEN IN TERMS OF MOLE FRACTIONS X_A ,X_B

$$X_A = \frac{N_A}{N_A + N_B} \qquad X_B = \frac{N_B}{N_A + N_B}$$

POLYMER SOLUTIONS AND BLENDS

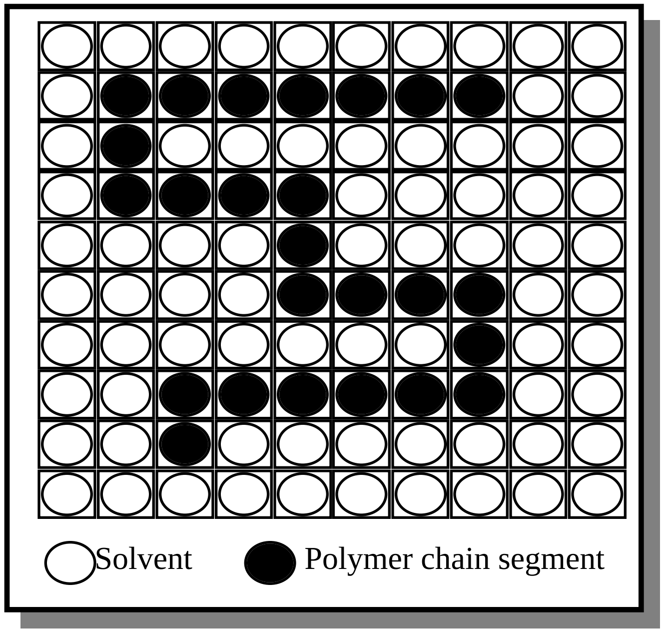


COUNTING THE CONFIGURATIONS IS MORE DIFFICULT, BUT FLORY AND HUGGINS OBTAINED;

$$-\frac{\Delta S_m}{R} = n_A \ln\varphi_A + n_B \ln\varphi_B$$

DEFINITION OF VOLUME FRACTIONS

$$-\frac{\Delta S_m}{R} = n_s \ln \varphi_s + n_p \ln \varphi_p$$



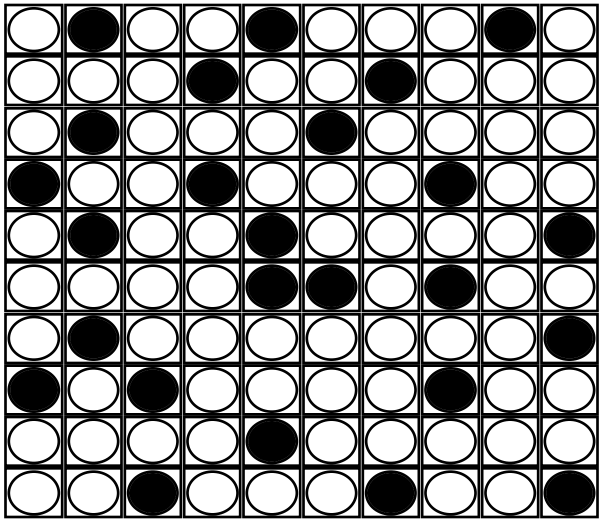
$$\varphi_s = \frac{n_s}{n_s + Mn_p}$$

75 / 100

$$\varphi_p = \frac{Mn_p}{n_s + Mn_p}$$

25/100

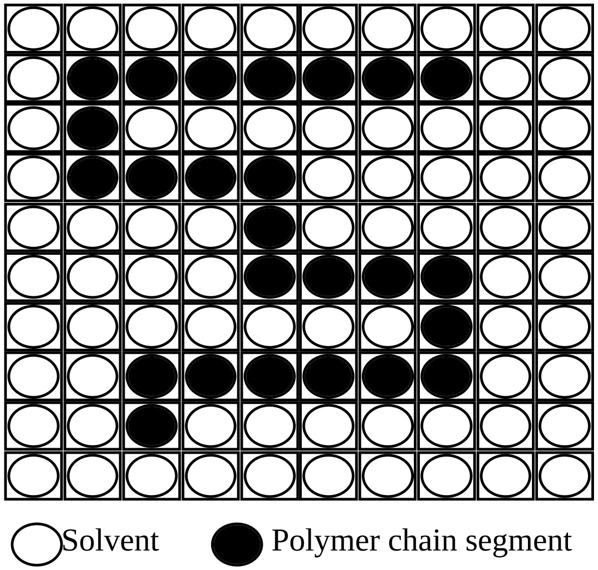
THE ENTROPY OF MIXING POLYMERS RELATIVE TO SMALL MOLECULES



$$\left[-\frac{\Delta S}{R}\right] = n_A \ln \varphi_A + n_B \ln \varphi_B$$

$n_A = 75$

$n_B = 25$



$$\left[-\frac{\Delta S}{R}\right] = n_A \ln \varphi_A + n_B \ln \varphi_B$$

$n_A = 75$

$n_B = 1$

THE ENTHALPY OF MIXING

The enthalpy of the system depends upon the interactions
Between the molecules - we need an expression for the
Change in enthalpy on going from the pure components
To the mixture

There are two related approaches that are most commonly
Used

Hildebrand - solubility parameters

Flory - χ parameter

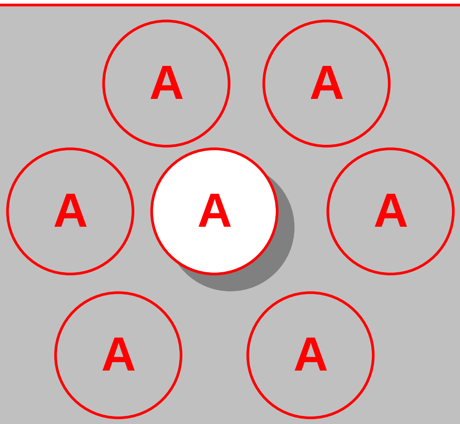
Both depend upon considering interactions
Between pairs of molecules and both assume
Dispersion and weak polar forces only

INTERACTIONS

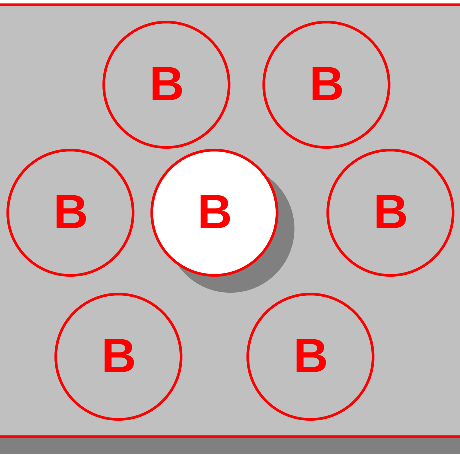
DISPERSION FORCES	Interaction energy $\sim \frac{1}{r^6}$
DIPOLE / DIPOLE (freely rotating)	
HYDROGEN BONDS and STRONG POLAR FORCES (charge transfer)	Interaction energy complicated,but short range
COULOMBIC (eg ionomers)	Interaction energy longer range $\sim 1/r$

COHESIVE ENERGY DENSITY

For the pure components,define the cohesive energyper pair of molecules as;

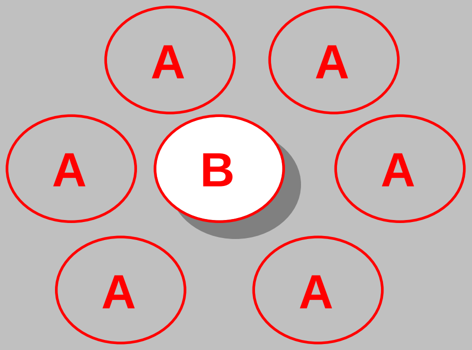


$$C_{AA} = \frac{\Delta E_{vap}}{V} \approx -P.E.$$



$$C_{BB} = \frac{\Delta E_{vap}}{V} \approx -P.E.$$

MIXTURES



Change in energy (per pair) related to

$$-[2C_{AB}-C_{AA}-C_{BB}]$$

Assume $C_{AB}=C_{AA}^{1/2}C_{BB}^{1/2}$

Obtain $[C_{AA}-2C_{AA}^{1/2}C_{BB}^{1/2}+C_{BB}]$

$$\longrightarrow \boxed{[C_{AA}^{1/2}-C_{BB}^{1/2}]^2}$$

The molar energy difference per pair on forming AB contacts from AA and BB contacts.Now multiply By the number of AB contacts in The mixture.But first,simplify !

SOLUBILITY PARAMETERS AND THE ENTHALPY OF MIXING

$$\delta_A = C_{AA}^{1/2}$$

$$\delta_B = C_{BB}^{1/2}$$

Define solubility parameters

$$(\delta_A - \delta_B)^2$$

The cohesive energy density change upon forming AB pairs from AA and BB pairs

Remember that this is per mole.To get the heat of mixing we must now multiply by the molar volume(to get an energy from the energy density),then the number of moles,then a factor that gives the number of AB contacts

$$\Delta H_m = (n_A + n_B)\, V_m\, \varphi_A\, \varphi_B\, (\delta_A - \delta_B)^2$$

FREE ENERGY OF MIXING- REGULAR SOLUTION THEORY

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

$$\frac{\Delta G_m}{RT} = n_A \ln X_A + n_B \ln X_B + (n_A + n_B) V_m \varphi_A \varphi_B (\delta_A - \delta_B)^2$$