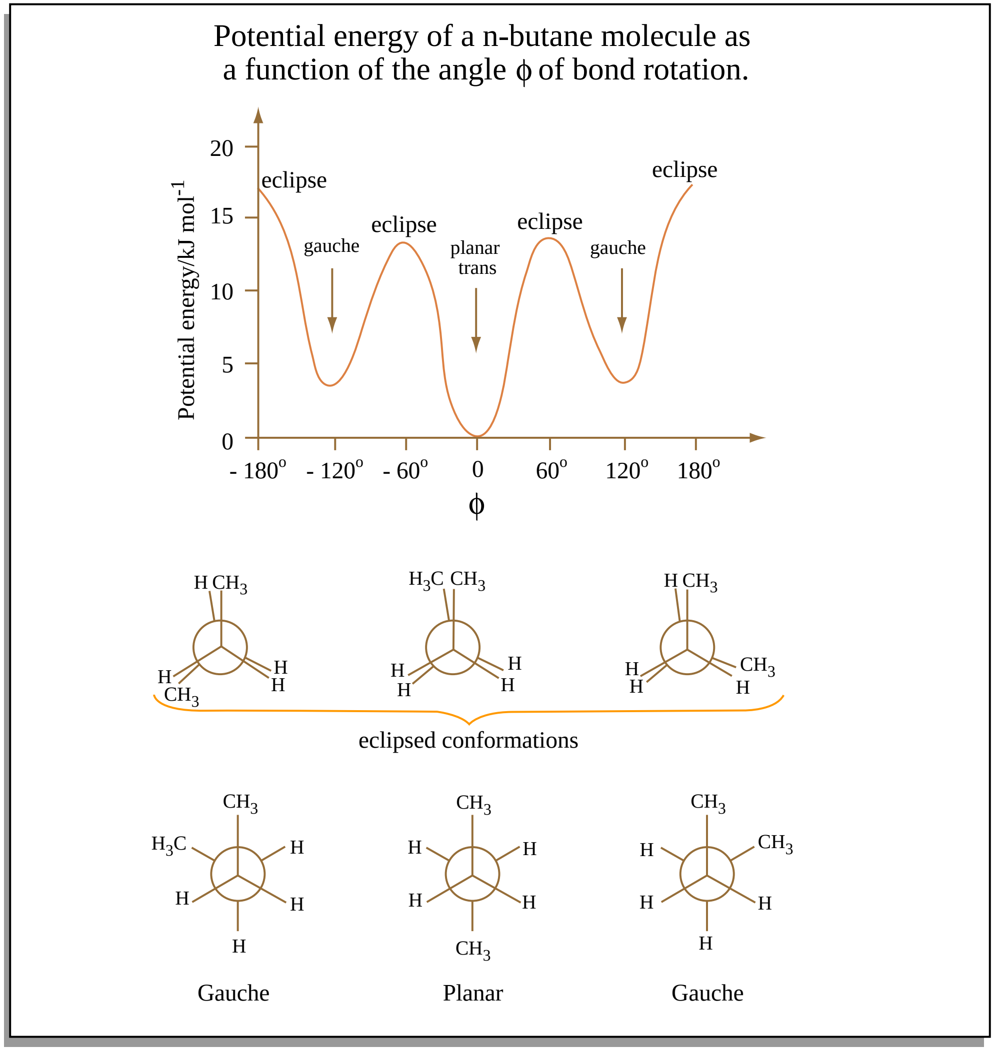
Example V(ϕ): Rotational conformations of n-butane

$CH_3CH_2CH_2CH_3$

$V(\phi)$



Potential energy of a n-butane molecule as a function of the angle ϕ of bond rotation.

Figure by MIT OCW.

Planar trans conformer is lowest energy

Views along the C2-C3 bond

High energy states

$V(\phi)$

Low energy states

Conformers: Rotational Isomeric State Model

- Rotational Potential V(ϕ)
  - Probability of rotation angle phi P(ϕ) ~ exp(-V(ϕ)/kT)
- Rotational Isomeric State (RIS) Model
  - e.g. Typical 3 state model : g^-, t, g^+ with weighted probabilities
  - Again need to evaluate $l_i \cdot l_{j+1}$ taking into account probability of a ϕ rotation between adjacent bonds
- This results in a bond angle rotation factor of $\frac{1+\langle\cos\phi\rangle}{1-\langle\cos\phi\rangle}$

combining

$$\langle r^2\rangle = nl^2\left(\left(\frac{1-\cos\theta}{1+\cos\theta}\right)\left(\frac{1+\langle\cos\phi\rangle}{1-\langle\cos\phi\rangle}\right)\right) = nl^2 C_\infty$$

where

$$C_\infty = \left(\left(\frac{1-\cos\theta}{1+\cos\theta}\right)\left(\frac{1+\langle\cos\phi\rangle}{1-\langle\cos\phi\rangle}\right)\right)$$

The so called "Characteristic ratio" and is compiled for various polymers

$$\langle\cos\phi\rangle = \frac{\int \cos(\phi)P(\phi)d\phi}{\int P(\phi)d\phi}$$

with P(ϕ) = exp(-V(ϕ)/kT)

The Chemist's Real Chain

- Preferred bond angles and rotation angles:
  - θ, ϕ. Specific bond angle θ between mainchain atoms (e.g. C-C bonds) with rotation angle chosen to avoid short range intra-chain interferences. In general, this is called "steric hindrance" and depends strongly on size/shape of set of pendant atoms to the main backbone (F, CH_3, phenyl etc).

- Excluded volume: self-crossing of chain is prohibited (unlike in diffusion or in the mathematician's chain model): Such excluded volume contacts tend to occur between more remote segments of the chain. The set of allowed conformations thus excludes those where the path crosses and this ***forces*** $\langle r_{l,n}^2 \rangle^{1/2}$ ***to increase***.

- Solvent quality: competition between the interactions of chain segments (monomers) with each other vs. solvent-solvent interactions vs. the interaction between the chain segments with solvent. ***Chain can expand or contract.***
  - monomer - monomer
  - solvent - solvent
  - monomer - solvent

$$\varepsilon_{M\text{-}M} \text{ vs. } \varepsilon_{S\text{-}S} \text{ vs. } \varepsilon_{M\text{-}S}$$

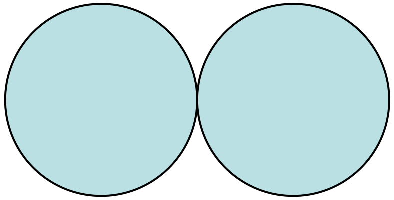
Excluded Volume

- **The excluded volume of a particle is that volume for which the center of mass of a 2nd particle is excluded from entering.**

- **<u>Example: interacting hard spheres of radius a</u>**
  - **volume of region denied to sphere A due to presence of sphere B**
  - **$V = 4/3\pi(2a)^3 = 8\ V_{sphere}$**

    but the excluded volume is shared by 2 spheres so

$$V_{excluded} = 4\ V_{sphere}$$



Solvent Quality and Chain Dimensions

Theta θ Solvent

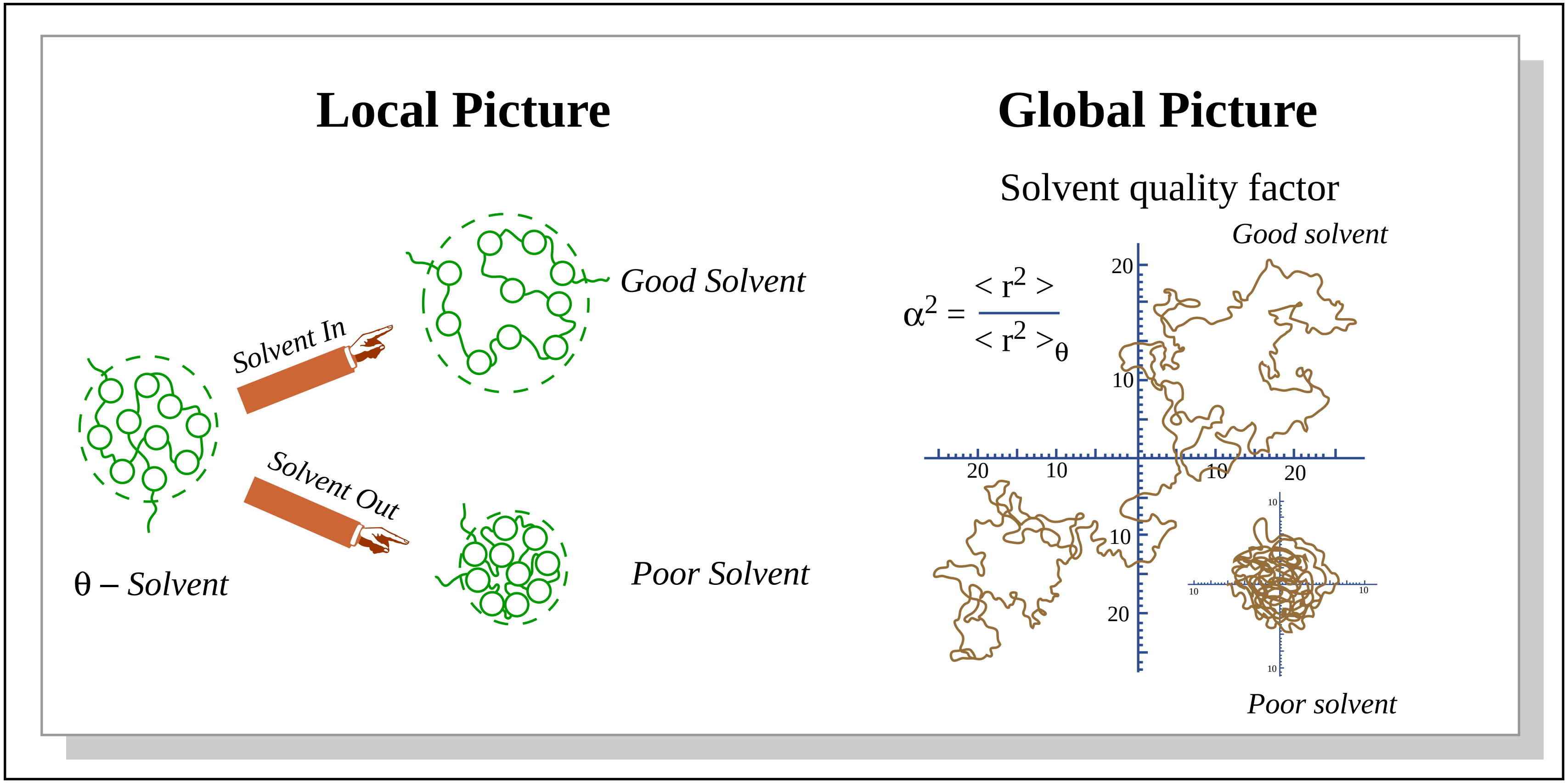


Figure by MIT OCW.

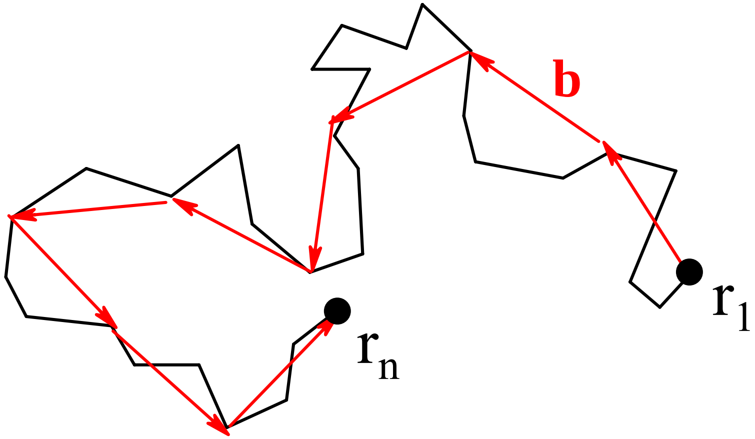
- Solvent quality:
  - M-M, S-S, M-S interactions: $\varepsilon_{M\text{-}M}$, $\varepsilon_{S\text{-}S}$, $\varepsilon_{M\text{-}S}$

Physicist's Universal Chain

- Recover random walk relation for real chain at theta condition (or in melt state!) by redefining a coarse grained model of N Kuhn steps

$$\langle r^2 \rangle^{1/2} = N^{1/2}\, b$$

Scaling law



N steps of length b,
b = Kuhn step

with $N = \frac{n}{C_\infty}$, $b = C_\infty \cdot l$

Fewer, larger steps

Manipulating $\{\vec{r}_{1n}\}$

To increase end to end distance

- **Excluded Volume (bigger, bulkier monomers)**
- **Large bond angle and strong steric interactions tend to favor all trans conformation** => C_∞ large

To increase or decrease end to end distance

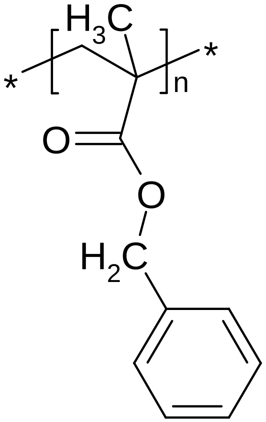
- **Solvent quality**
- **Temperature** (affects solvent quality and relative interaction energies)
- **Deformation** (stretch the coil: rubber elastic behavior)

Characteristic Ratio

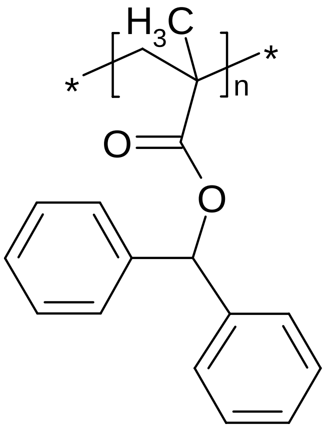
Experimentally measure MW and hence chain dimensions
(technique: laser light scattering: Zimm plot)
in a theta solvent for high MW sample

$$C_\infty = \frac{\langle r^2 \rangle_\theta}{nl^2}$$

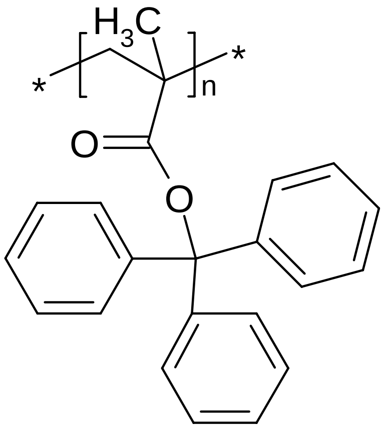
Influence of steric interactions on characteristic ratio



$C_\infty = 10$



$C_\infty = 14$



$C_\infty = 20.3$

Summary: Flexible Coil Chain Dimensions

Model	**$\langle r^2 \rangle$**	**Comments**
Mathematician's Ideal RW	$\langle r^2 \rangle = nl^2$	Freely jointed chain, n bonds each of length 1.
Chemist's Real Chain θ fixed , V(ϕ)-RIS	$\langle r^2 \rangle = nl^2 \left(\left(\frac{1-\cos\theta}{1+\cos\theta} \right) \left(\frac{1+\overline{\cos\phi}}{1-\overline{\cos\phi}} \right) \right)$ $\langle r^2 \rangle_\theta = nl^2 C_\infty$	Allow preferred bond angles and preferred rotation angles about main chain bonds Characteristic ratio takes into account all local steric interactions
Real Chain θ, V(ϕ) – and solvent quality and excluded volume	$\langle r^2 \rangle = nl^2 C_\infty \alpha^2$	Factor α takes into account solvent quality and long range chain self-intersections (excluded volume) $\alpha^2 = \frac{\langle \boldsymbol{r}^2 \rangle}{\langle \boldsymbol{r}^2 \rangle_\theta}$: α = 1 for two states: (i) Theta condition - particular solvent and temperature (ii) Melt state
Physicist's Universal Chain (α = 1 conditions)	$\langle r^2 \rangle = Nb^2$ where N = # of statistical segments, b = statistical segment length, $b = C_\infty l$	C_∞ is incorporated into Kuhn length b.

Thermodynamics of Polymer Solutions

- <u>Bragg-Williams Lattice Theory for Phase Behavior of Binary Alloys</u>

  W. L. Bragg and E. J. Williams, Proc. Roy. Soc. A145, 699 (1934); *ibid* A151, 540 (1935).

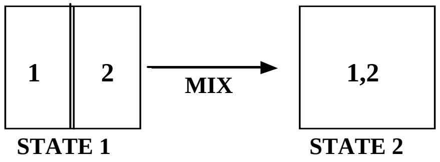
- Generalize to polymer-polymer and polymer-solvent phase behavior.

  P. J. Flory, J. Chem Phys. 10, 51 (1942), M. L. Huggins, J. Phys. Chem. 46, 151 (1942).

Chapter 3, Young and Lovell

$$G = H - TS$$

$$\Delta G = G_{1,2} - (G_1 + G_2)$$



Binary Component System in State 2

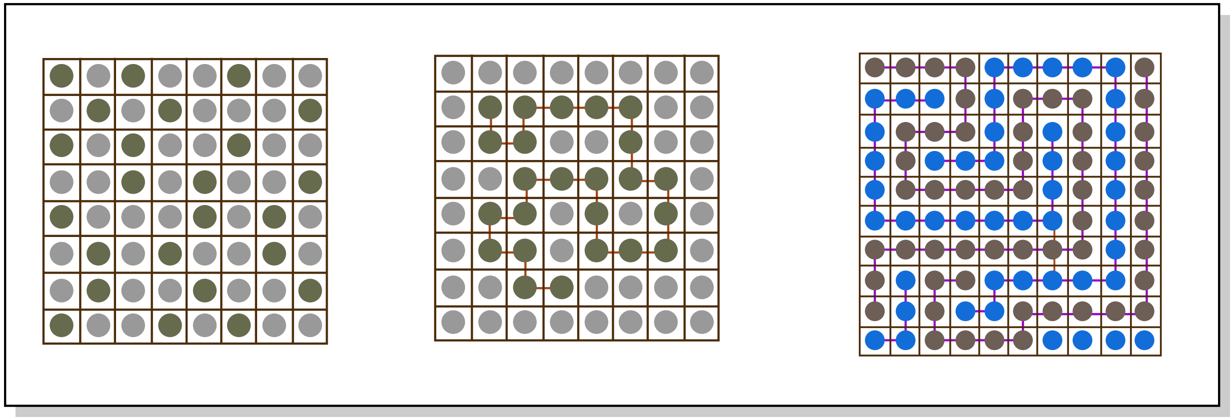


Figure by MIT OCW.

solvent-solvent solvent-polymer polymer-polymer

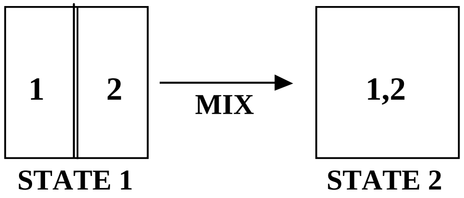
Materials scientists already familiar with B-W Lattice Theory !

new situations

Thermodynamics of Polymer Sol’n cont’d

$$G = H - TS$$

$$\Delta G = G_{1,2} - (G_1 + G_2)$$



- State 1 – 2 pure phases comprised of n_i moles of component i

  If component is a polymer, it has x_i segments and each segment has volume v_i

$$V_1 = n_1 x_1 v_1 \qquad V_2 = n_2 x_2 v_2$$

- State 2 – mixed phase,

  assume

$$V = n_1 x_1 v_1 + n_2 x_2 v_2 \qquad \Delta V_{1,2} = 0$$

Note if system is comprised of a solvent and a polymer, the convention is to name the solvent component 1 and the polymer component 2

Thermodynamics cont'd – Entropy

1. Translational - (sometimes called combinatorial or configurational) due to the number of distinguishable spatial arrangements
2. Conformational - due to number of distinguishable shapes of a given molecule keeping center of mass fixed. We will assume that there are no differences in molecular conformations in the unmixed vs. mixed state.
3. Recall $S = k \ln \Omega$ $\Delta S = k \ln \Omega_{1,2} - k(\ln \Omega_1 + \ln \Omega_2)$
4. $\Omega_1 = 1$, $\Omega_2 = 1$ since there is only 1 way to arrange a pure component in its volume

- The increase in translational entropy is due to the increased total volume available to the molecules in the mixed state. The statistical mechanics is standard for mixing of 2 gases:

$$\Delta S_m = k \ln \Omega_{1,2} - 0$$

$$\Delta S_m = k(n_1 \ln V / V_1 + n_2 \ln V / V_2)$$

Mean Field Lattice Theory

- Mean field: the interactions between molecules are assumed to be due to the interaction of a given molecule and an *average field* due to all the other molecules in the system. To aid in modeling, the solution is imagined to be divided into a set of cells within which molecules or parts of molecules can be placed (lattice theory).

- The total volume, V, is divided into a lattice of N_o cells, each cell of volume v. The molecules occupy the sites randomly according to a probability based on their respective volume fractions. To model a polymer chain, one occupies x_i adjacent cells.

$$N_o = N_1 + N_2 = n_1 x_1 + n_2 x_2$$

$$V = N_o v$$

- Following the standard treatment for small molecules ($x_1 = x_2 = 1$)

$$\Omega_{1,2} = \frac{N_0!}{N_1! N_2!}$$

using Stirling's approximation: $\ln M! = M \ln M - M \quad \text{for } M >> 1$

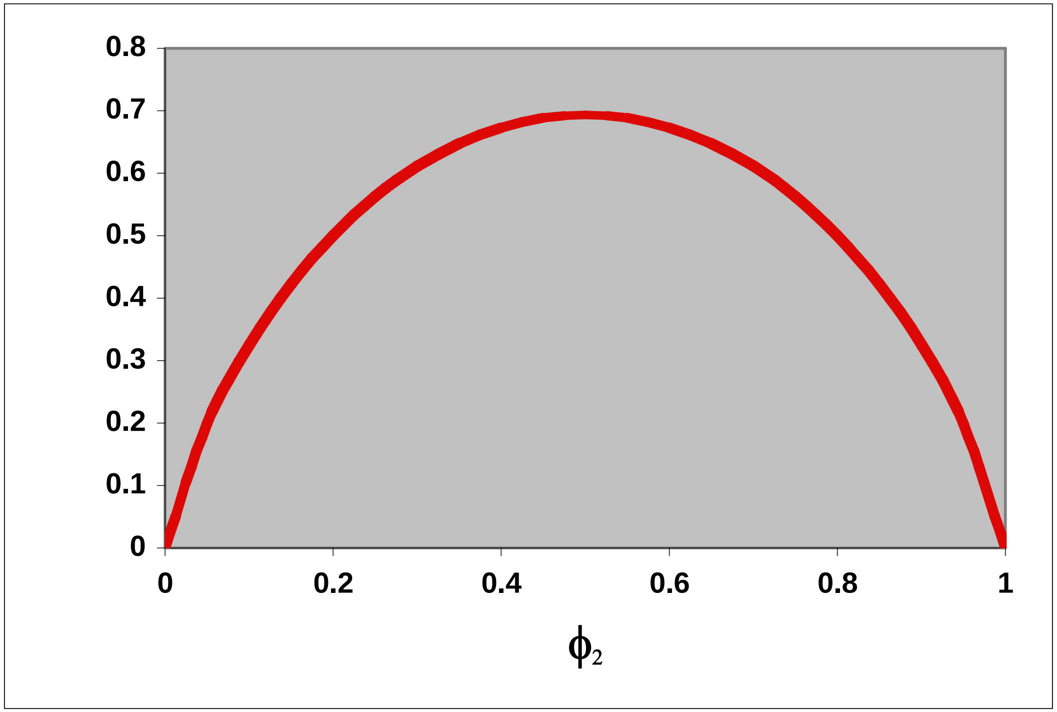
$$\Delta S_m = k(-N_1 \ln \phi_1 - N_2 \ln \phi_2)$$

$\phi_1 = ?$

Entropy Change on Mixing ΔS_m is :

$$\frac{\Delta S_m}{N_o} = +k(-\phi_1 \ln \phi_1 - \phi_2 \ln \phi_2)$$

Remember this is for small molecules
$x_1 = x_2 = 1$



Note the symmetry

The entropic contribution to ΔG_m is thus seen to always favor mixing if the random mixing approximation is used.

Enthalpy of Mixing ΔH_m

- Assume lattice has *z* nearest-neighbor cells.
- To calculate the enthalpic interactions we consider the number of *pairwise* interactions. The probability of finding adjacent cells filled by component *i*, and *j* is given by assuming the probability that a given cell is occupied by species *i* is equal to the volume fraction of that species: ϕ_i.

ΔH_m cont'd

$$\upsilon_{ij} = \text{ \# of i,j interactions}$$

$$\upsilon_{12} = N_1 z \phi_2$$

$$\upsilon_{11} = N_1 z \phi_1 / 2$$

$$\upsilon_{22} = N_2 z \phi_2 / 2$$

Mixed state enthalpic interactions

$$H_{1,2} = \upsilon_{12}\,\varepsilon_{12} + \upsilon_{11}\,\varepsilon_{11} + \upsilon_{22}\,\varepsilon_{22}$$

$$H_{1,2} = z\,N_1\,\phi_2\,\varepsilon_{12} + \frac{z}{2} N_1\,\phi_1\,\varepsilon_{11} + \frac{z}{2} N_2\,\phi_2\,\varepsilon_{22}$$

Pure state enthalpic interactions

$$H_1 = \frac{z\,N_1}{2}\varepsilon_{11} \qquad H_2 = \frac{z\,N_2}{2}\varepsilon_{22}$$

$$\Delta H_M = z\left\lfloor N_1\phi_2\varepsilon_{12} + \frac{N_1\varepsilon_{11}}{2}(\phi_1 - 1) + \frac{N_2\varepsilon_{22}}{2}(\phi_2 - 1)\right\rfloor$$

recall

$$N_1 + N_2 = N_0$$

Some math

$$\Delta H_M = z\,N_0\left[\varepsilon_{12} - \frac{1}{2}(\varepsilon_{11} + \varepsilon_{22})\right]\phi_1\phi_2$$

Note the symmetry

χ Parameter

- Define χ:

$$\chi = \frac{z}{kT}\left[\varepsilon_{12} - \frac{1}{2}\left(\varepsilon_{11} + \varepsilon_{22}\right)\right]$$

χ represents the chemical interaction between the components

$$\frac{\Delta H_M}{N_0} = k\,T\,\chi\,\phi_1\,\phi_2$$

- ΔG_M :

$$\Delta G_M = \Delta H_M - T\,\Delta S_M$$

$$\frac{\Delta G_M}{N_0} = kT\,\chi\phi_1\phi_2 - kT\left[-\phi_1\ln\phi_1 - \phi_2\ln\phi_2\right]$$

$$\frac{\Delta G_M}{N_0} = kT\left[\chi\phi_1\phi_2 + \phi_1\ln\phi_1 + \phi_2\ln\phi_2\right]$$

Note: ΔG_M is symmetric in ϕ_1 and ϕ_2.

This is the Bragg-Williams result for the change in free energy for the mixing of binary metal alloys.

$\Delta G_M(T, \phi, \chi)$

- Flory showed how to pack chains onto a lattice and correctly evaluate $\Omega_{1,2}$ for polymer-solvent and polymer-polymer systems. Flory made a complex derivation but got a very simple and intuitive result, namely that ΔS_M is decreased by factor (1/*x*) due to connectivity of *x* segments into a single molecule:

$$\frac{\Delta S_M}{N_0} = -k\left[\frac{\phi_1}{x_1}\ln\phi_1 + \frac{\phi_2}{x_2}\ln\phi_2\right]$$

For polymers

- **Systems of Interest**

- solvent – solvent	$x_1 = x_2 = 1$	
- solvent – polymer	$x_1 = 1$	$x_2 =$ large
- polymer – polymer	$x_1 =$ large,	$x_2 =$ large

$$\boxed{\frac{\Delta G_M}{N_0} = kT\left[\chi\phi_1\phi_2 + \frac{\phi_1}{x_1}\ln\phi_1 + \frac{\phi_2}{x_2}\ln\phi_2\right]}$$

Note possible huge asymmetry in x_1, x_2

$$\chi = \frac{z}{kT}\left[\varepsilon_{12} - \frac{1}{2}\left(\varepsilon_{11} + \varepsilon_{22}\right)\right]$$

Need to examine variation of ΔG_M with T, χ, ϕ_i, and x_i to determine phase behavior.