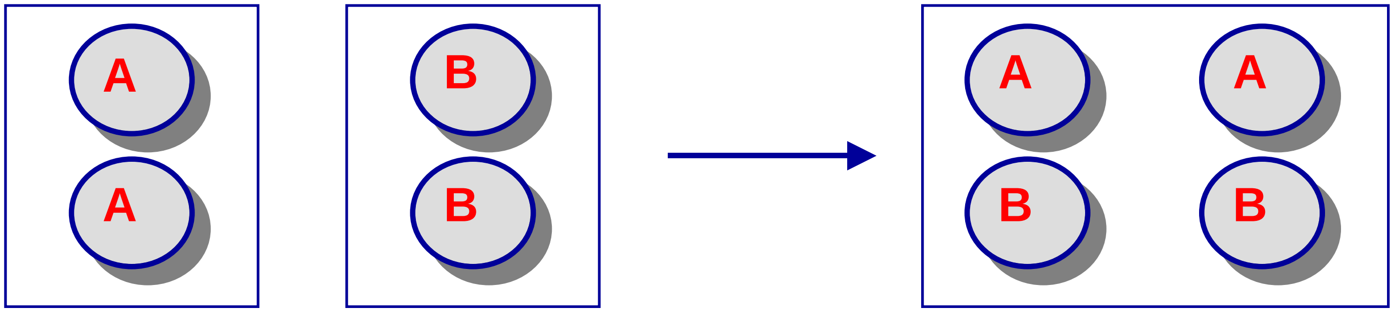
THE FLORY χ PARAMETER



$$\Delta w_{AB} = \frac{1}{2}(w_{AA} + w_{BB}) - w_{AB}$$

Energy change per AB contact

$$\chi_A = \Delta w_{AB}\, z/RT$$

Energy difference (/RT) between an A molecule
Surrounded by other A's,and one surrounded by B's

$$\Delta H_m = n_A \varphi_B (RT\chi_A)$$

Heat of mixing (multiply energy difference
By the number of AB contacts)

FREE ENERGY OF MIXING- FLORY - HUGGINS THEORY

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

$$\frac{\Delta G_m}{RT} = \boxed{n_A \ln \varphi_A + n_B \ln \varphi_B} + \boxed{n_A \varphi_B \chi}$$

ENTROPIC TERM

ENTHALPIC TERM

RELATIONSHIP BETWEEN χ AND SOLUBILITY PARAMETERS

The expressions for the heat of mixing are equivalent

$$\Delta H_m = N_s \varphi_p (RT\chi)$$

$$\Delta H_m = V_m(n_s + n_p)(\delta_s - \delta_p)^2 \varphi_s \varphi_p$$

Using $\varphi_s = \frac{n_s V_s}{V_m}$

Then $\chi = \frac{V_s}{RT}(\delta_s - \delta_p)^2$

But, experimentally for solutions **(not blends)**

$$\chi \sim 0.34 + \frac{V_s}{RT}(\delta_s - \delta_p)^2$$

WHY MOST SIMPLE HYDROCARBON POLYMERS DON'T MIX

$$\frac{\Delta G_m}{RT} = \boxed{n_A \ln \varphi_A + n_B \ln \varphi_B} + n_A \varphi_B \chi$$

Interaction term
- Positive

Combinatorial entropy
- Small

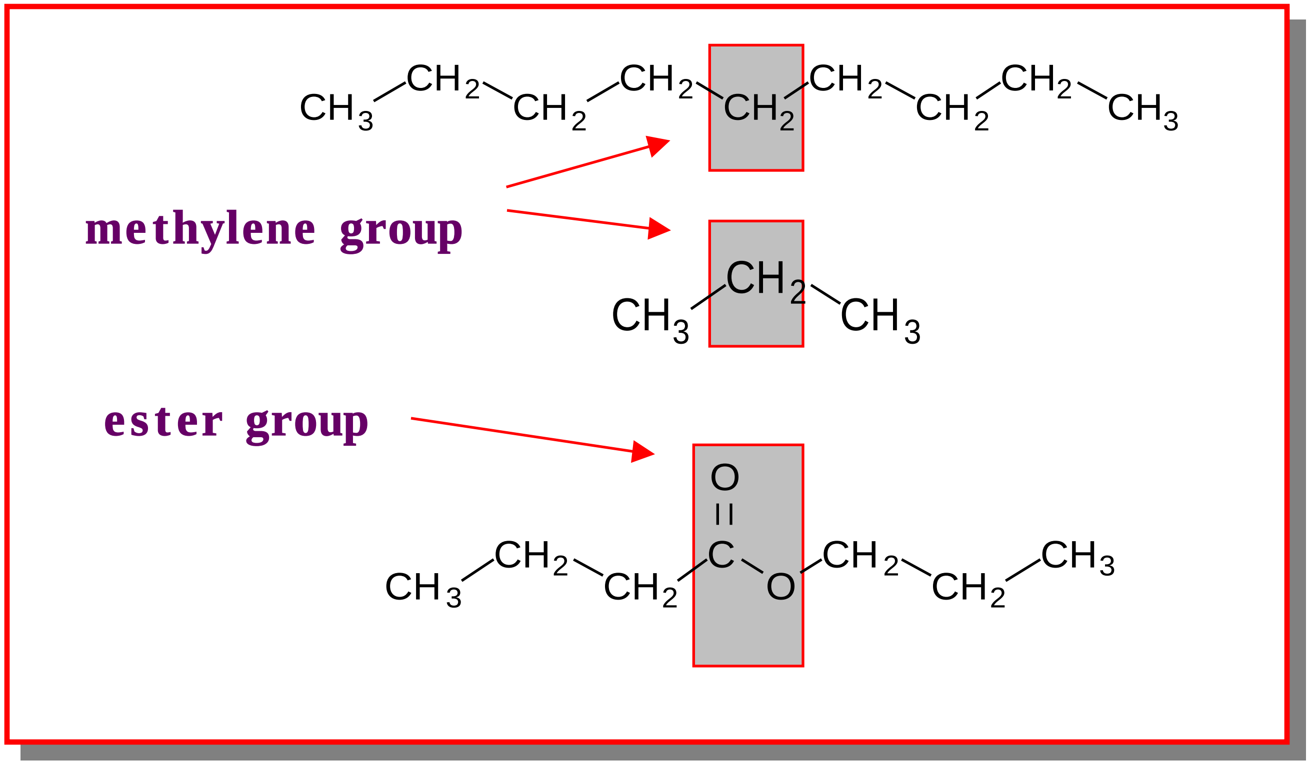
$$\boxed{\chi = \frac{V_{ref}}{RT}[\delta_A - \delta_B]^2}$$

To obtain a miscible system we must
Have specific interactions

SOLUBILITY PARAMETERS OF POLYMERS

- **Cannot be obtained from energy of vaporization measurements**

- **Use group contributions**



methylene group

ester group

SOME LIMITATIONS OF THE FLORY - HUGGINS THEORY

1. BASED ON A LATTICE MODEL THAT USES VARIOUS APPROXIMATIONS IN THE “COUNTING’ PROCESS
2. IGNORES "FREE VOLUME"
3. ASSUMES RANDOM MIXING OF CHAINS IN CALCULATING THE ENTROPY AND SEGMENTS IN CALCULATING THE ENTHALPY
4. STRICTLY,ONLY APPLIES TO NON - POLAR MOLECULES
5. ONLY ACCOUNTS FOR COMBINATORIAL ENTROPY

PHASE BEHAVIOUR

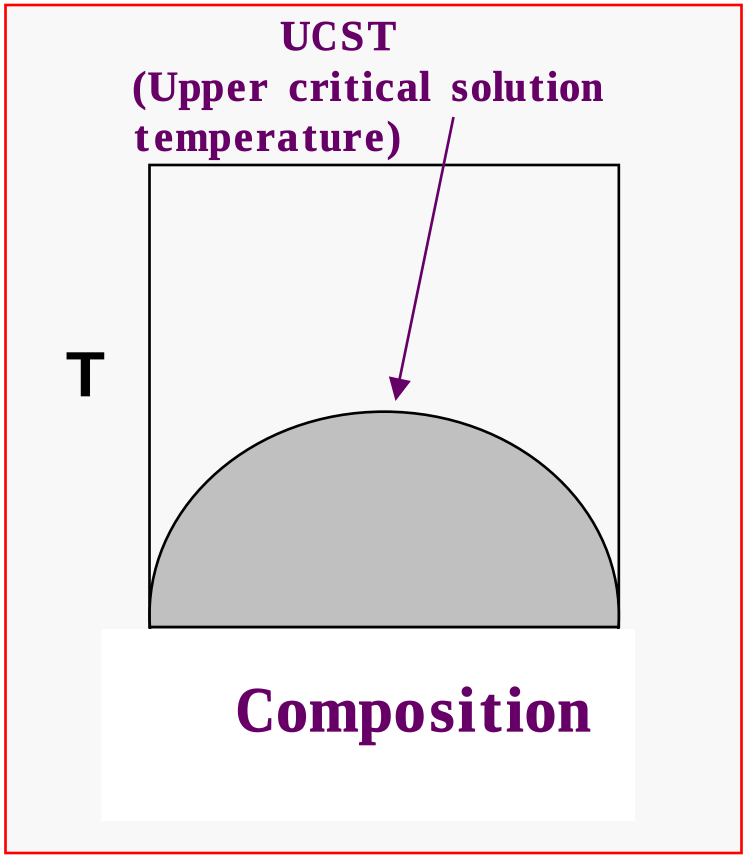
RECALL THAT

$$\chi = \frac{V_s}{RT}(\delta_s - \delta_p)^2$$

Hence χ increases **with decreasing temperature**

Accordingly,one might expect that as the temperature of a solution (or blend) is lowered, there comes a point where the free energy becomes positive and phase separation occurs.

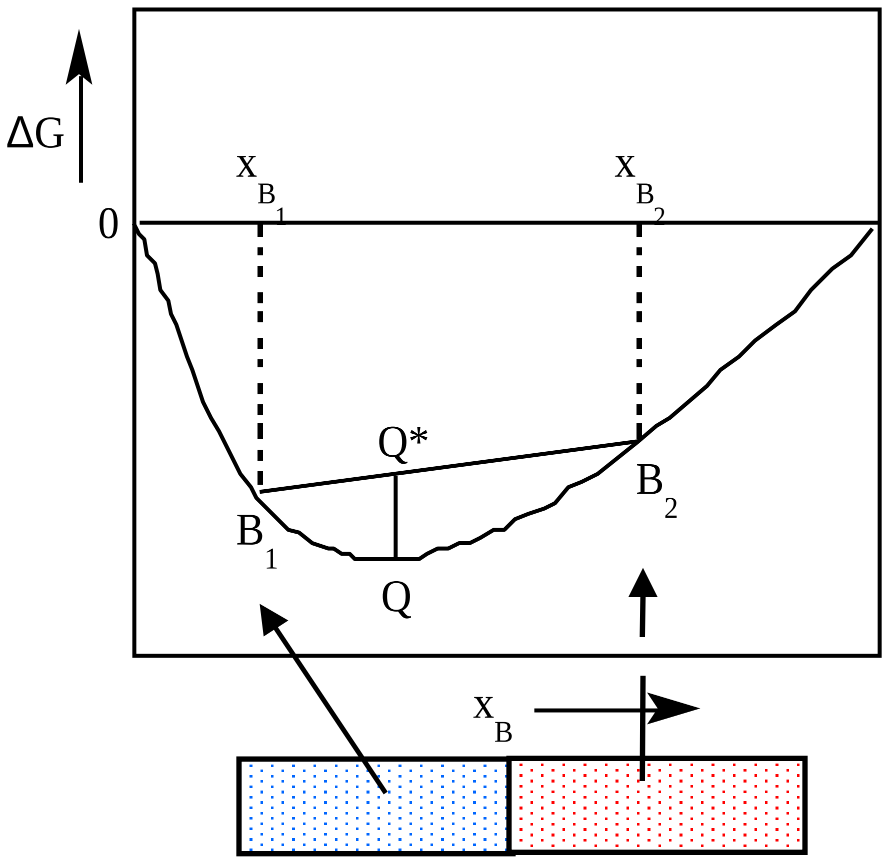
Schematically, the phase diagram **would look like**



PHASE BEHAVIOUR

However, the free energy does not have to be positive in order to have phase separation !!!

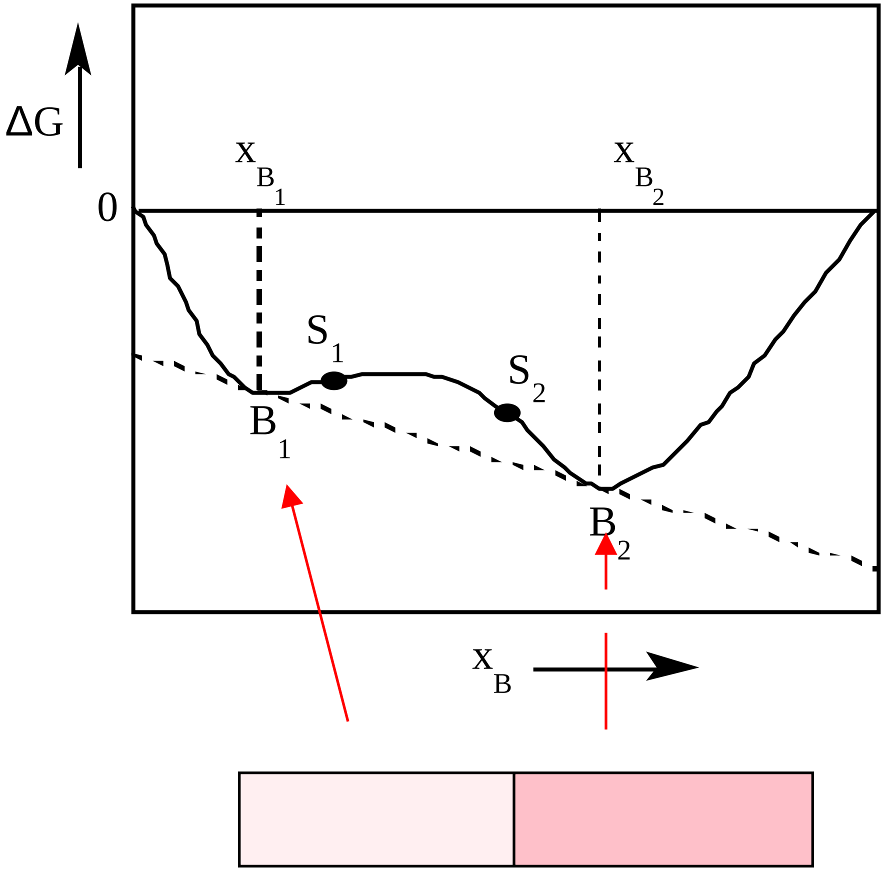
The shape of the free energy / Composition curve is crucial



IF THE BARRIER IS REMOVED, WOULD THE TWO SOLUTIONS MIX?

EVEN MORE PHASE BEHAVIOUR

WHAT IF THE FREE ENERGY CURVE LOOKED LIKE THIS ?

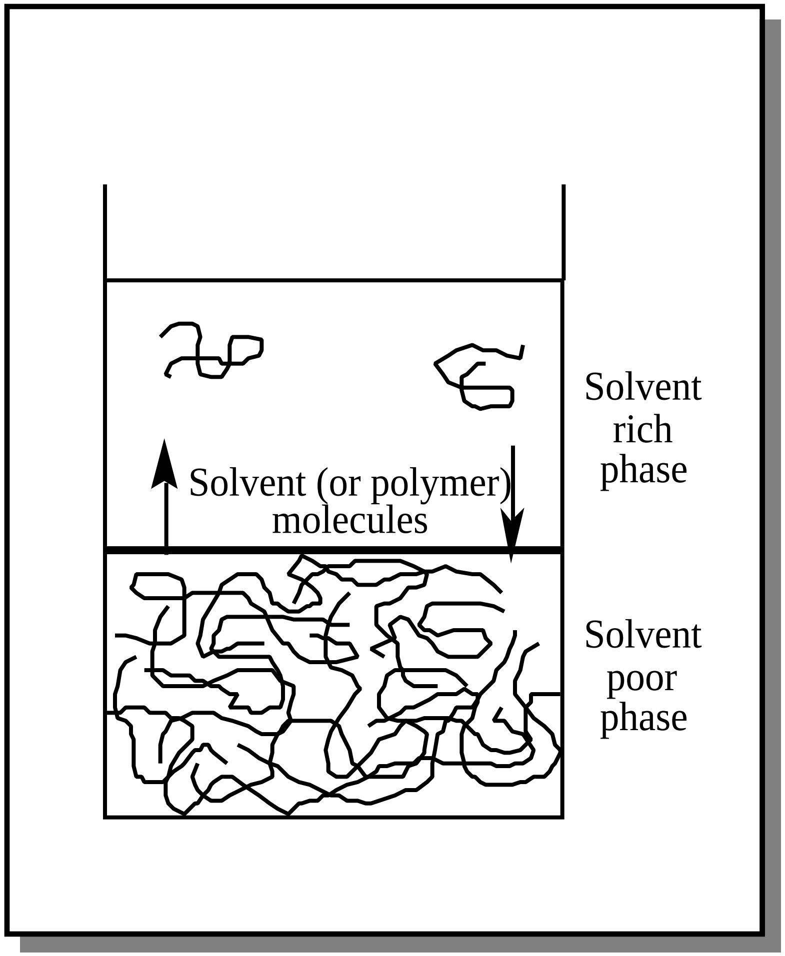


CHEMICAL POTENTIAL

FROM THE FLORY - HUGGINS EQUATION;

$$\frac{\mu_s - \mu_s^o}{RT} = \frac{\partial(\Delta G_m/RT)}{\partial N_s}$$

$$= \ln(1 - \varphi_p) + \left(1 - \frac{1}{M}\right)\varphi_p + \varphi_p^2 \chi$$

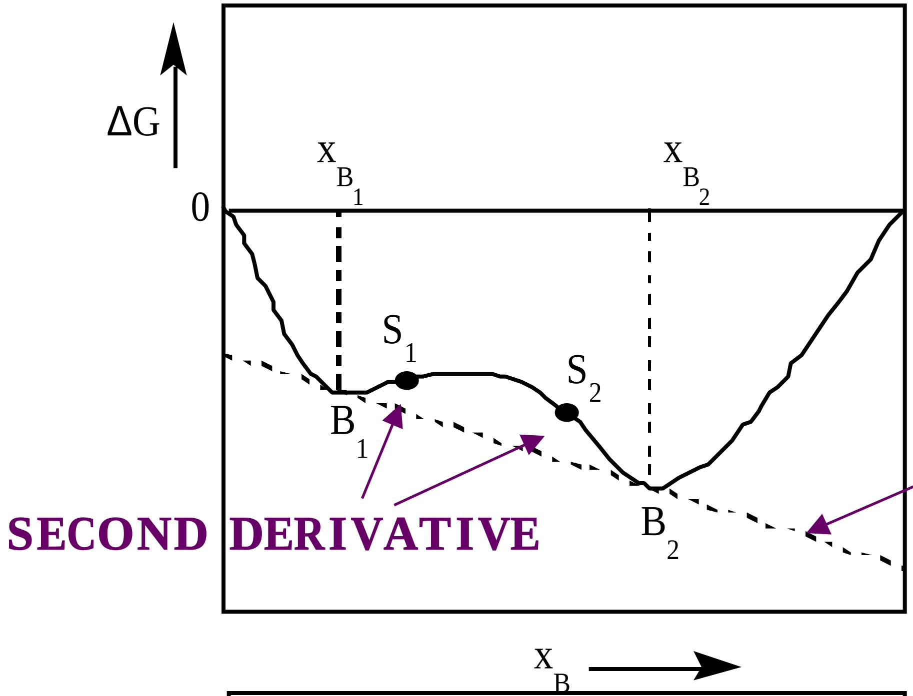


Solvent (or polymer) molecules

Solvent rich phase

Solvent poor phase

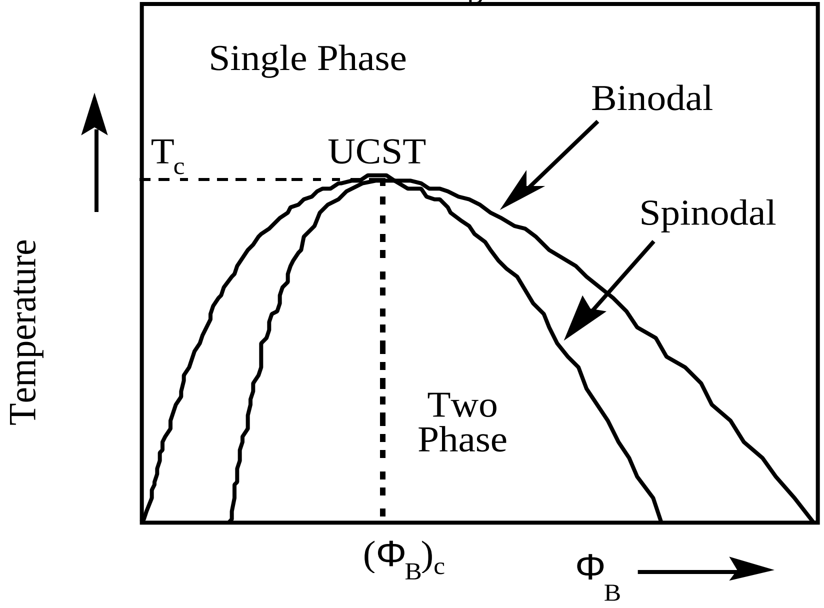
CALCULATING A PHASE DIAGRAM



SECOND DERIVATIVE

FREE ENERGY CURVE AT A GIVEN T

FIRST DERIVATIVE OF FREE ENERGY WITH RESPECT TO COMPOSITION (chemical potential)



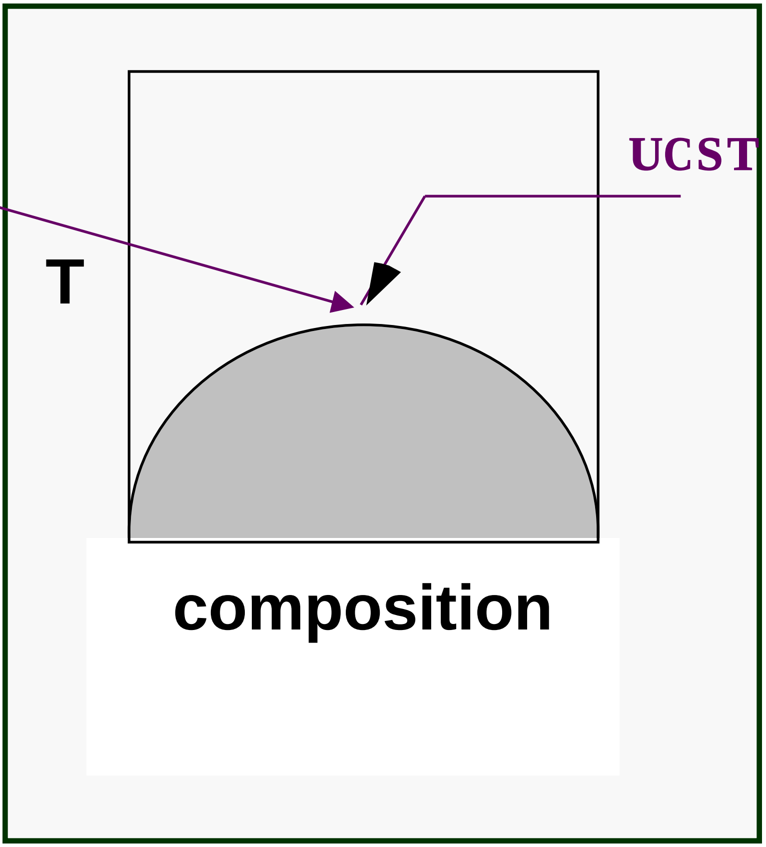
COLLECTING ALL THE POINTS FROM FREE ENERGY CURVES CALCULATED AT VARIOUS TEMPERATURES

THE CRITICAL VALUE OF χ

DEFINED BY

$$\frac{\partial^2(\Delta G_m)}{\partial \varphi_s^2} = 0$$

$$\frac{\partial^3(\Delta G_m)}{\partial \varphi_s^3} = 0$$



However,we can also start from The chemical potential and differentiate succesively to obtain

$$\frac{1}{(1-\varphi_p)} - \left(1 - \frac{1}{M}\right) - 2\varphi_p\chi = 0$$

$$\frac{1}{(1-\varphi_p)^2} - 2\chi = 0$$

FOR SOLUTIONS $\chi_c = \frac{1}{2}\left[1 + \frac{1}{M_s^{1/2}}\right]^2 \sim 0.5$

FOR BLENDS $\chi_c = \frac{1}{2}\left[\frac{1}{M_A^{1/2}} + \frac{1}{M_B^{1/2}}\right]^2 \sim$ very small

CRITICAL VALUE OF THE SOLUBILITY PARAMETER DIFFERENCE

RECALL THAT

$$\chi \sim 0.34 + \frac{V_s}{RT}(\delta_s - \delta_p)^2$$

THEN IF V_s /RT ~1/6

$$\delta_s - \delta_p \sim \{(0.5 - 0.34)\, 6\}^{1/2} \sim 0.98$$

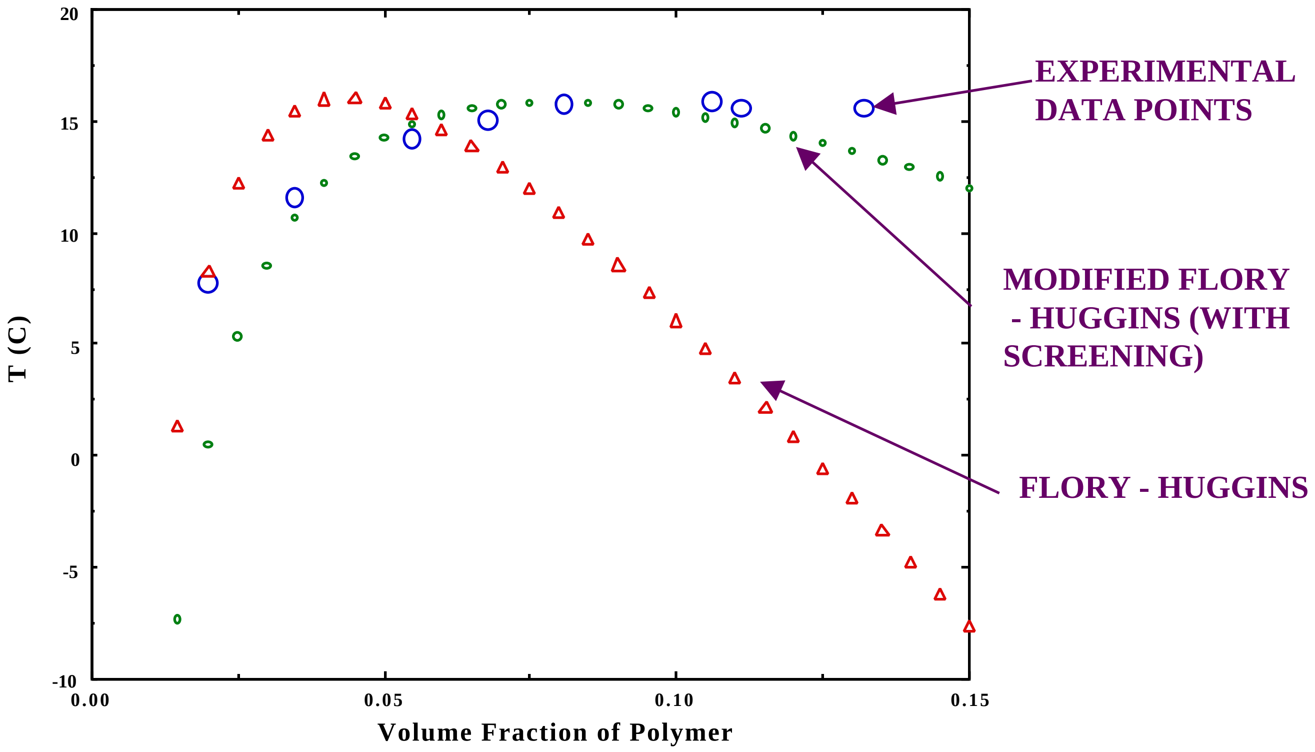
HENCE

$$\boxed{\delta_s - \delta_p < 1}$$

OR, MORE PRECISELY

$$\boxed{\Delta\delta_c = \pm 1}$$

SPINODAL FOR POLYSTYRENE - CYCLOHEXANE

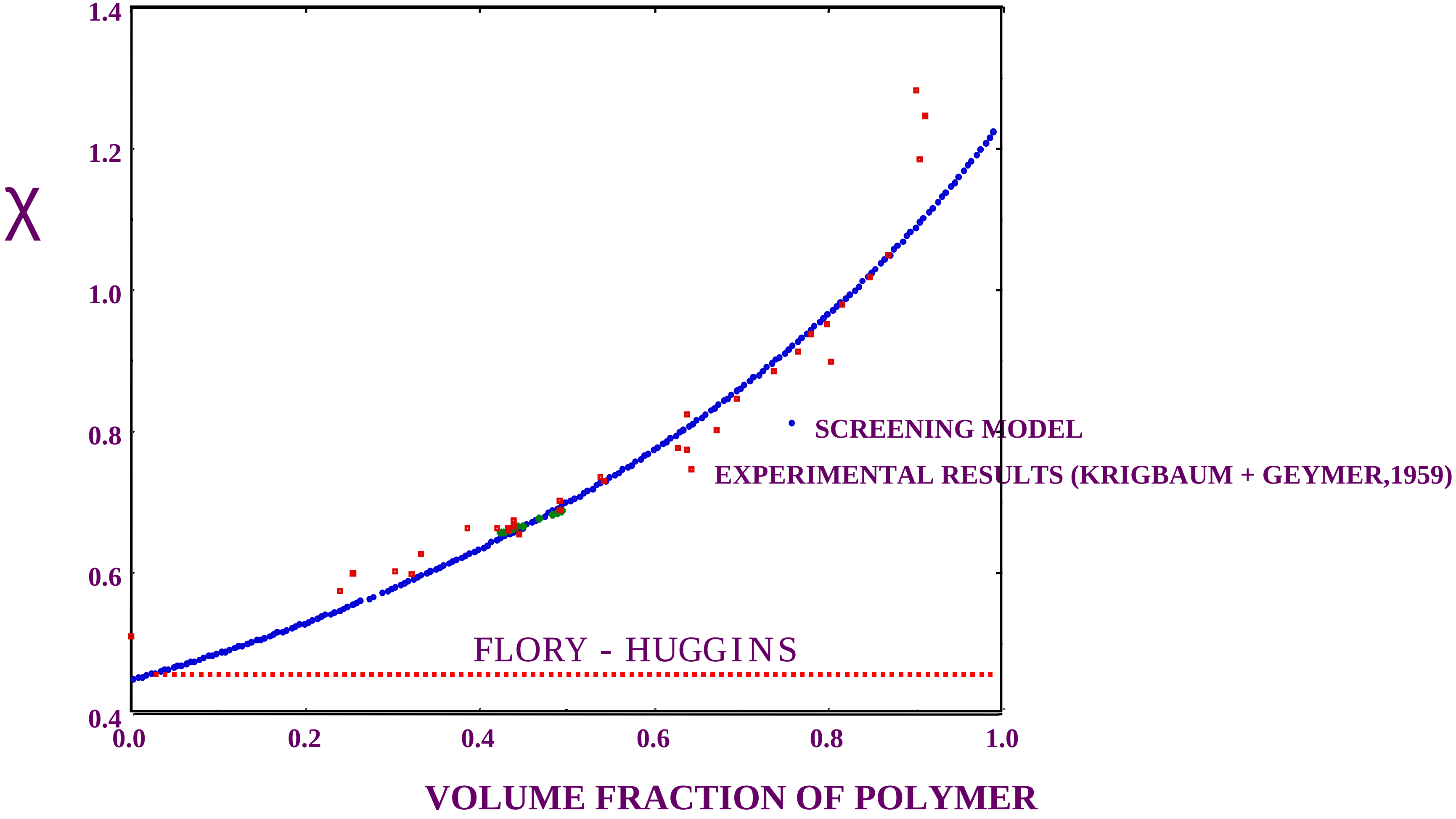


EXPERIMENTAL DATA POINTS

MODIFIED FLORY - HUGGINS (WITH SCREENING)

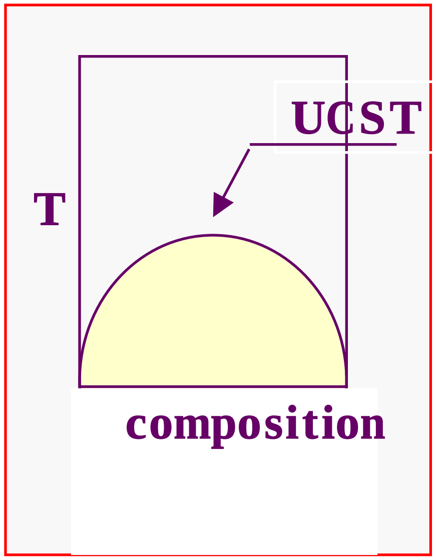
FLORY - HUGGINS

VALUES OF χ FOR SOLUTIONS OF POLYSTYRENE IN CYCLOHEXANE

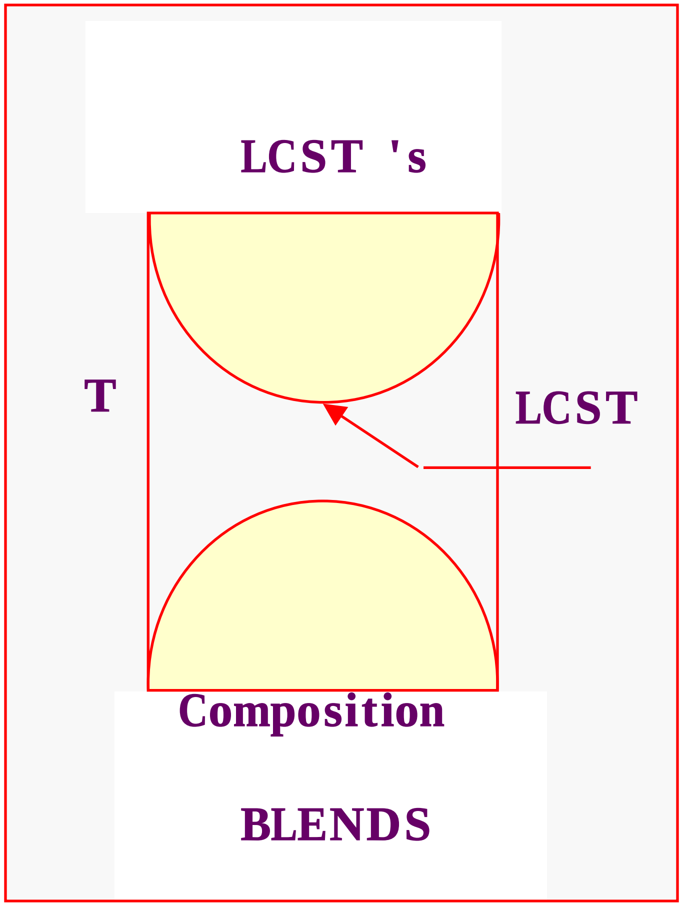


PREDICTIONS OF SIMPLE MODEL

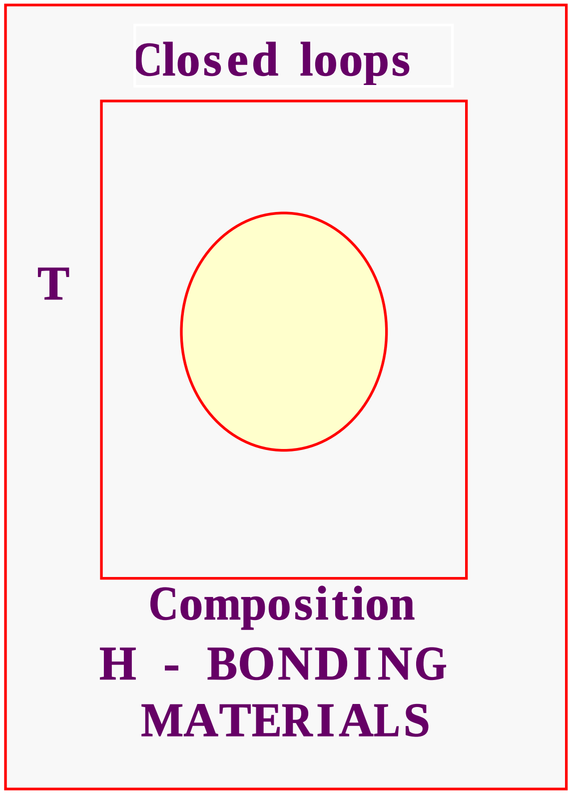
1. Most polymers won't mix
2. UCST phase behaviour



OBSERVED BEHAVIOUR

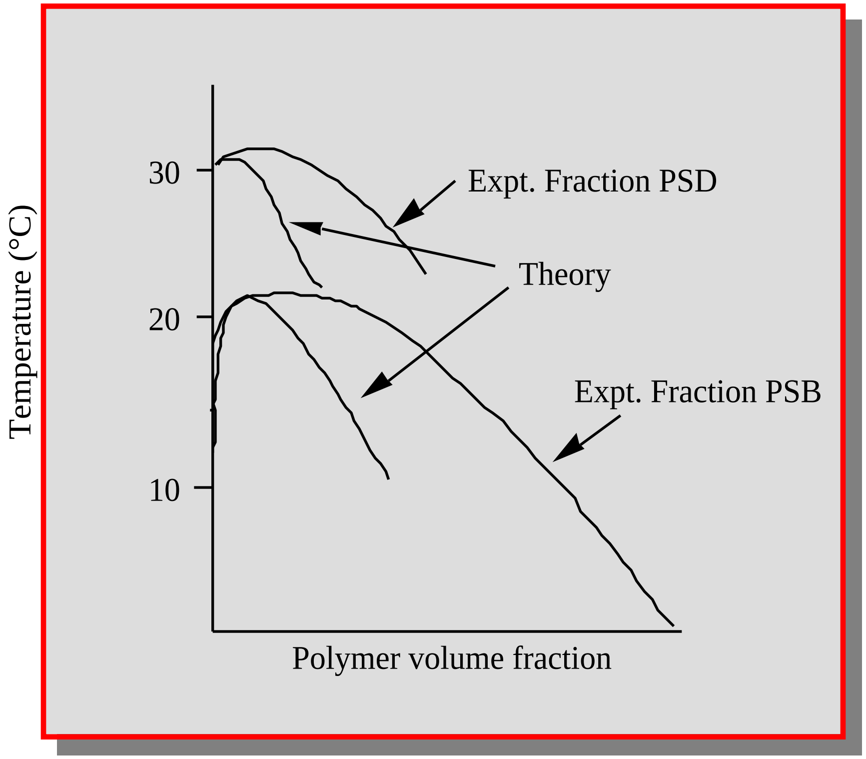


BLENDS

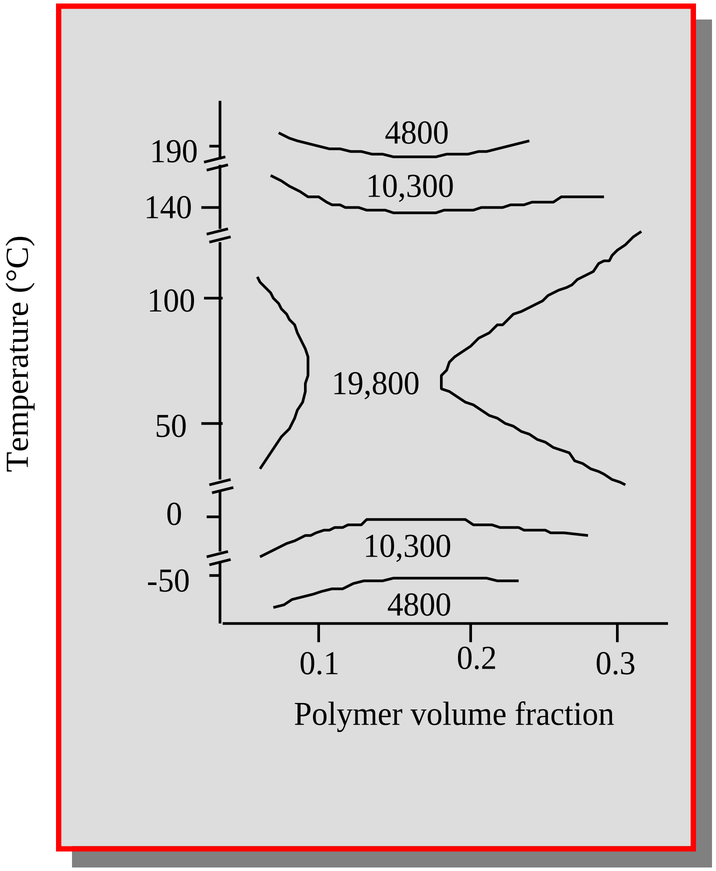


H - BONDING MATERIALS

COMPARISON TO EXPERIMENT

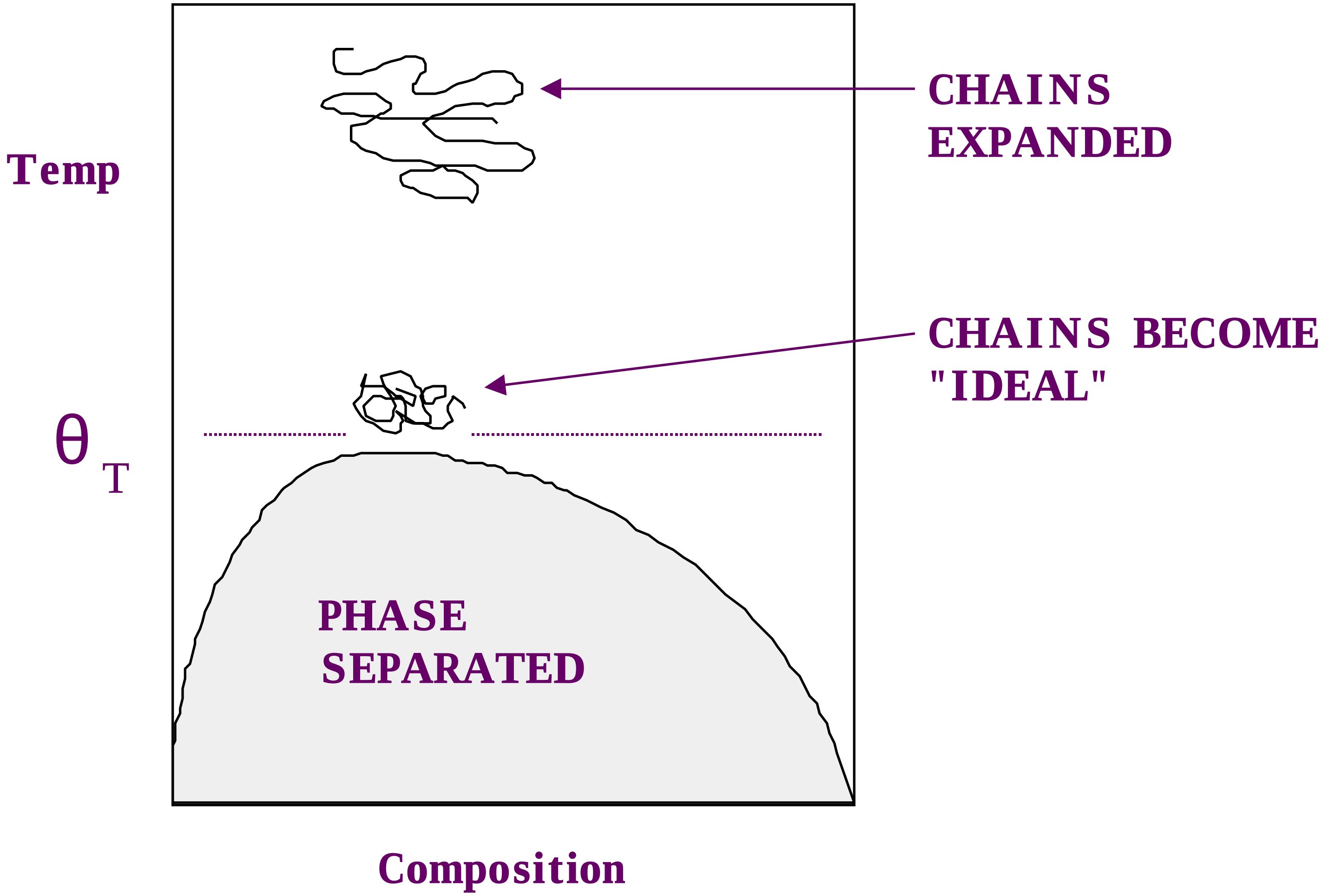


SHULTZ AND FLORY



SIOW ET AL

THE θ TEMPERATURE



Temp

CHAINS
EXPANDED

CHAINS BECOME
"IDEAL"

θ_T

PHASE
SEPARATED

Composition