

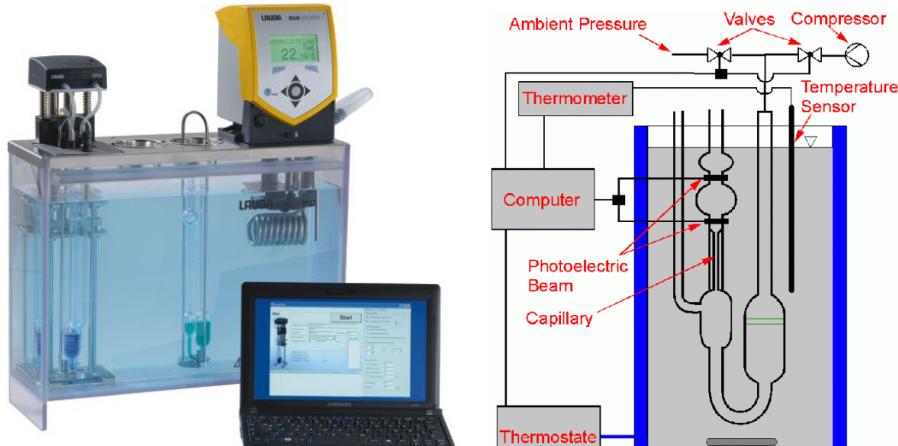
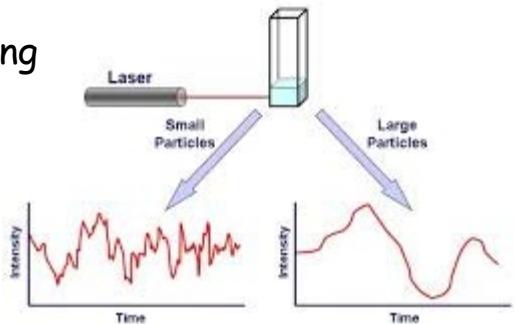
## Dilute Solution

- Polymers are characterized by molecular weight distribution and polydispersity
- The polymer industry needs a rapid molecular weight determination because all properties of polymers change with the molecular weight

# Introduction: Why dilute solution ?



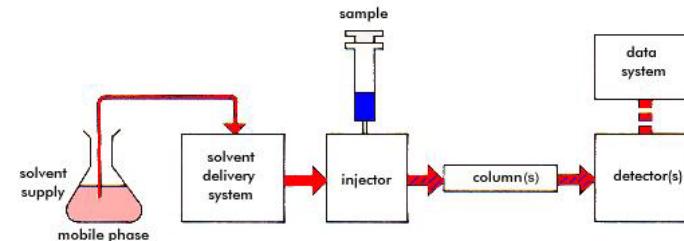
Light Scattering



Viscometry



GPC (Gel Permeation Chromatography)  
is today the most important method

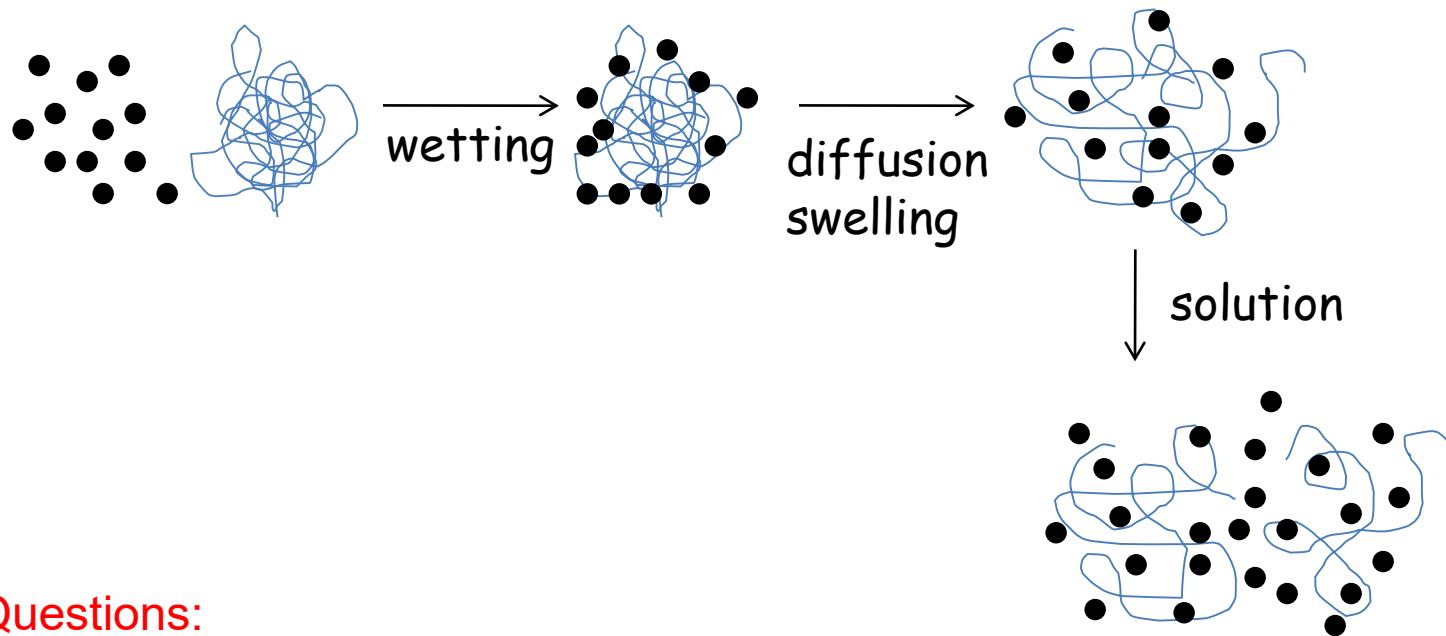


**requirement:**  
a solution, where the single chains  
are separated by solvent molecules

→ DILUTE SOLUTION

# How does a polymer dissolve?

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## Questions:

1. When and why do polymers dissolve?
2. How is the structure in solution?
3. How we can determine the molecular weight?

# Outline

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## 1. When and why do polymers dissolve?

→ Thermodynamics of dilute polymer solutions

Solubility parameter

Statistical Thermodynamics of Mixing – Lattice Model-

- ideal solution
- regular solution
- polymer solution -Flory-Huggins Theory -

# Solubility Parameter

One of the simplest notions in chemistry is that “like dissolves like”

- Qualitatively, “like” may be defined variously in terms of similar chemical groups or similar polarities
- Quantitatively, a parameter named **solubility parameter**  $\delta$  can be defined:

$$\delta = \left( \frac{\Delta E}{V} \right)^{1/2}$$

$\frac{\Delta E}{V}$  cohesive energy density

Energy required to vaporize 1 cm<sup>3</sup> of a sample at zero pressure [given in cal/cm<sup>3</sup>].

$$\Delta H_M = V_M \left[ \left( \frac{\Delta E}{V_P} \right)^{1/2} - \left( \frac{\Delta E}{V_S} \right)^{1/2} \right]^2 \nu_S \nu_P$$

$V_M$  = total volume of the mixture

$\Delta E$  = energy of vaporization to a gas at  $p = 0$

$V$  = molar volume of the components, for both species 1 (S) and 2 (P)

$\nu$  = volume fraction of component 1 (s) and 2 (p) in the mixture

$$\Delta H_M = V_M (\delta_{Polymer} - \delta_{Solvent})^2 \nu_1 \nu_2$$

Solubility parameters should be similar to one another in order for dissolution to occur

# Solubility Parameters of Common Solvents/Polymers

## Solubility parameters of common solvents

Table 3.1 Solubility parameters of some common solvents

Solvent	$\delta(\text{cal}/\text{cm}^3)^{1/2}$	H-bonding <sup>a</sup>	Group	Specific Gravity <sup>b</sup> $20^\circ\text{C} (\text{g}/\text{cm}^3)$
Acetone	9.9		m	0.7899
Benzene	9.2		p	0.87865
n-Butyl acetate	8.3		m	0.8825
Carbon tetrachloride	8.6		p	1.5940
Cyclohexane	8.2		p	0.7785
n-Decane	6.6		p	—
Dibutyl amine	8.1		s	—
Difluorodichloromethane	5.1		p	—
1,4-Dioxane	10.0		m	1.0337
Low odor mineral spirits	6.9		p	—
Methanol	14.5		s	0.7914
Toluene	8.9		p	0.8669
Turpentine	8.1		p	—
Water	23.4		s	0.99823
Xylene	8.8		p	0.8611

Source: J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, 2nd ed., Wiley-Interscience, New York, 1975, Sec. IV.

<sup>a</sup>Hydrogen bonding is an important secondary parameter in predicting solubility. p, Poorly H-bonded; m, moderately H-bonded; and s, strongly H-bonded.

<sup>b</sup>J. Brandrup and E. H. Immergut, *Polymer Handbook*, 3rd ed., Wiley-Interscience, New York, 1989, Sec. III, p. 29.

## Solubility parameters of common polymers

Table 3.2 Solubility parameters and densities of common polymers (2)

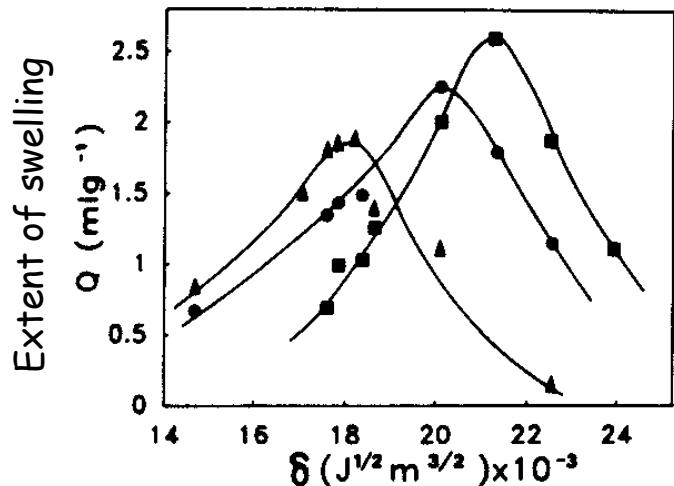
Polymer	$\delta(\text{cal}/\text{cm}^3)^{1/2}$	Density(g/cm <sup>3</sup> )
Polybutadiene	8.4 <sup>a</sup>	1.01
Polyethylene	7.9	0.85 (amorphous)
Poly(methyl methacrylate)	9.45	1.188
Polytetrafluoroethylene	6.2	2.00 amorphous, estimated
Polyisobutene	7.85	0.917
Polystyrene	9.10	1.06
Cellulose triacetate	13.60	1.28 <sup>b</sup>
Cellulose tributyrate	—	1.16 <sup>b</sup>
Nylon 66	13.6	1.24
Poly(ethylene oxide)	9.9	1.20
Poly(vinyl chloride)	9.6	1.39

<sup>a</sup>Note:  $1(\text{cal}/\text{cm}^3)^{1/2} = 2.046 \times 10^3 (\text{J}/\text{m}^3)^{1/2}$ .

<sup>b</sup>C. J. Malm, C. R. Fordyce, and H. A. Tanner, *Ind. Eng. Chem.*, **34**, 430 (1942).

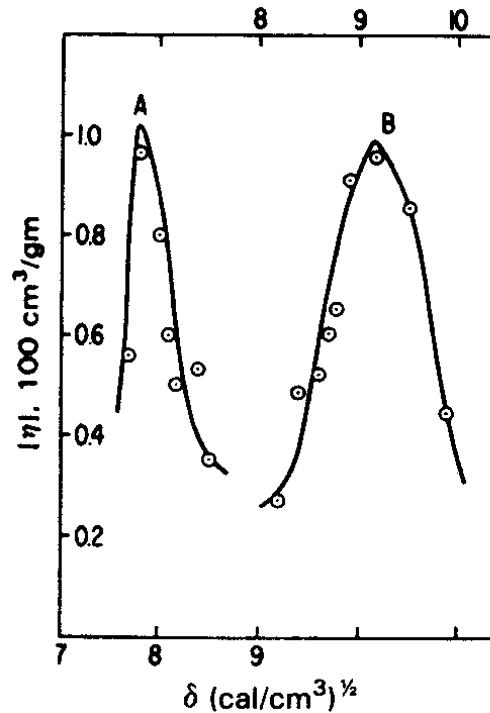
# Experimental Determination of Solubility Parameters

## Crosslinked Polymers



**Figure 3.1** The swelling coefficient,  $Q$ , reaches a maximum when the solubility parameter of the solvent nearly matches that of the polymer, for several cross-linked systems: polyurethane (■), polystyrene (▲), and a polyurethane – polystyrene interpenetrating polymer networks (●) (5).

## Linear or Branched Polymers



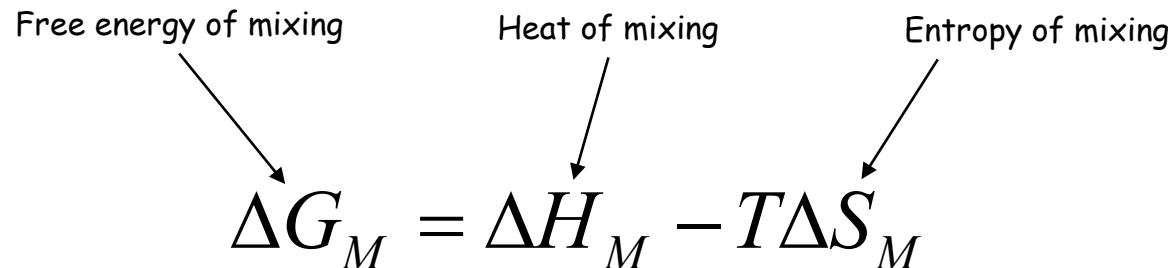
**Figure 3.2** Determination of the solubility parameter, using the intrinsic viscosity method (4), for polyisobutene (A) and polystyrene (B). The intrinsic viscosity,  $[\eta]$ , is a measure of the individual chain size. See Section 3.8.

# Solution Behavior: free energy of mixing

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

Free energy of mixing      Heat of mixing      Entropy of mixing



> or <:

$\Delta G_M \text{ } \textcolor{blue}{<} 0$  solution process occurs spontaneously

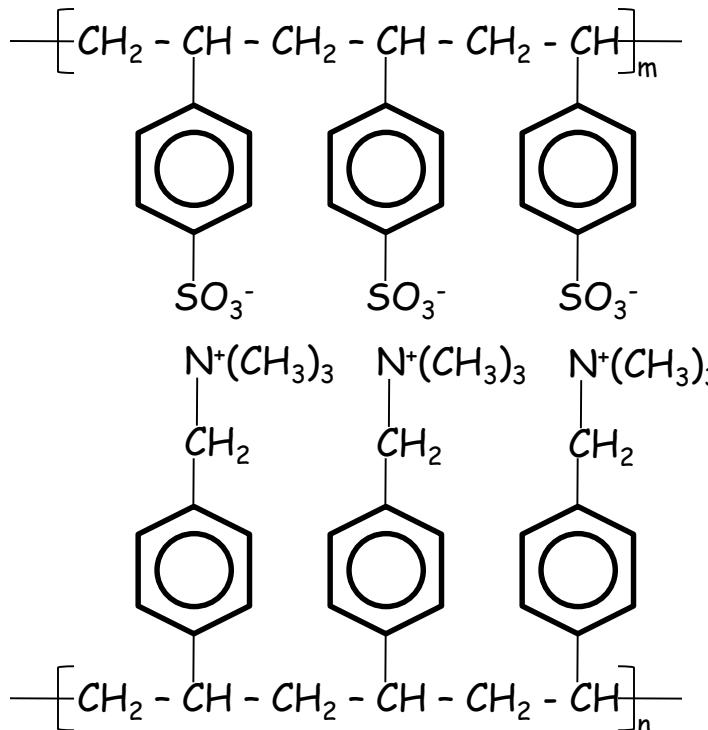
$T\Delta S_M \text{ } \textcolor{blue}{>} 0$  always increasing of entropy

$\Delta H_M \text{ } \textcolor{blue}{>} 0$  usually positive for relatively nonpolar organic compounds, is important

# Example of negative enthalpie

$$\Delta H_M < 0$$

when two species attract one another, perhaps by having opposite polarities, being acid and base relative to one another, or through hydrogen bonding

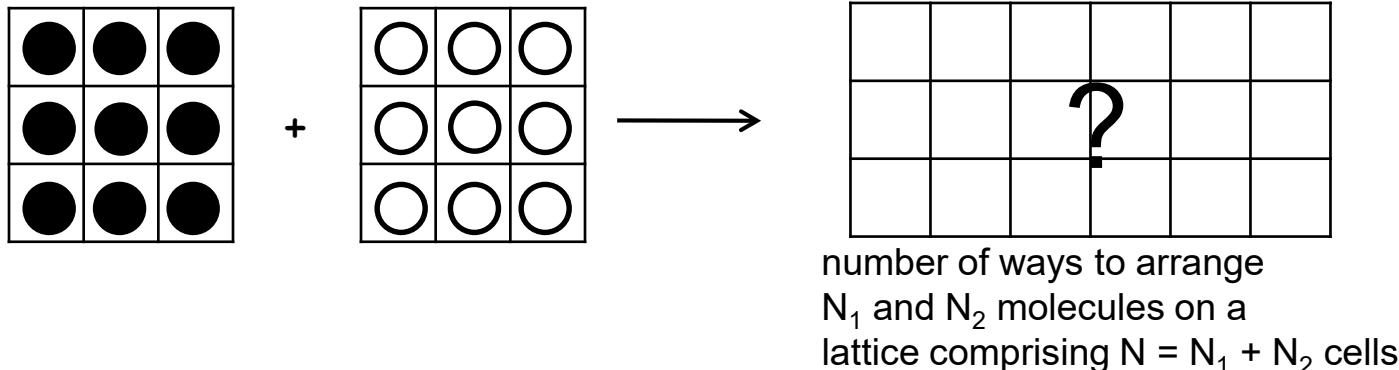


Sodium polystyrene sulfonate (polyanion)

Poly(vinyl benzyl trimethylammonium chloride) (polycation)

# Statistical Thermodynamics: The Lattice Model

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Mixing of two substances 1 and 2 results in a change of

- enthalpy,
- entropy
- volume

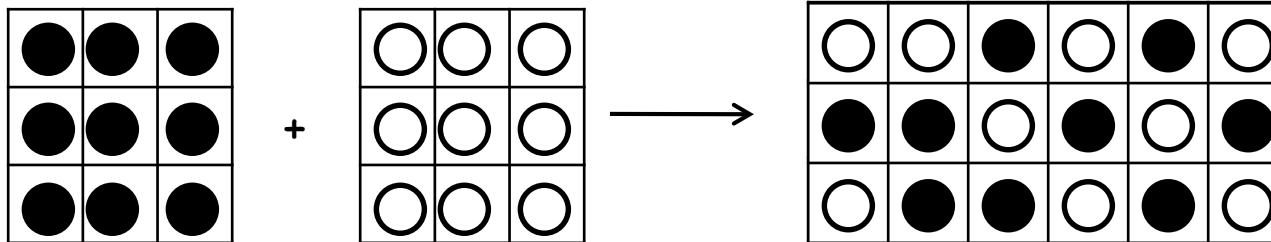
In ideal case volumes are additive

$N_0$  number of places in the lattice  $N_0 = N_1 + N_2$

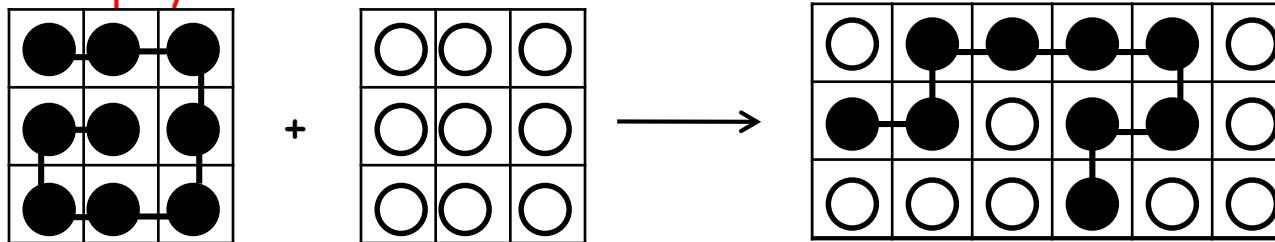
Every place is occupied with 1 or 2

# The Lattice Model

small molecule mixture

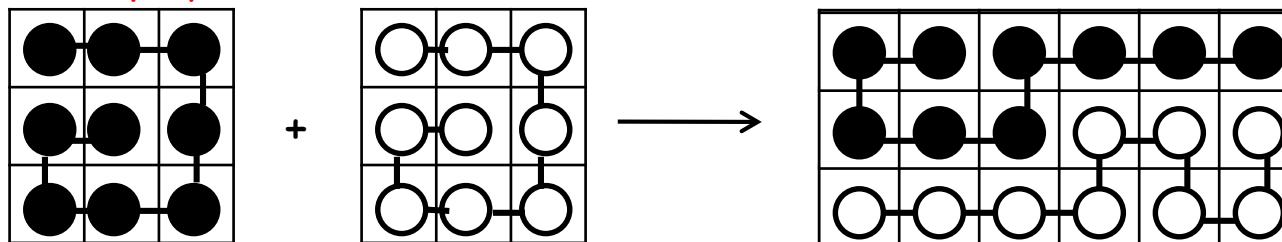


polymer solution



The polymer (1) is divided in  $x$  segments, each of which is assumed to occupy the same volume as a solvent molecule (2)

polymer mixture



Compared to small molecules, polymers have a smaller number of possible arrangements they can adopt  $\rightarrow \Omega$  is generally small

# Case 1: Ideal Solutions ( $\Delta H_M = 0$ )

small molecule mixture

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

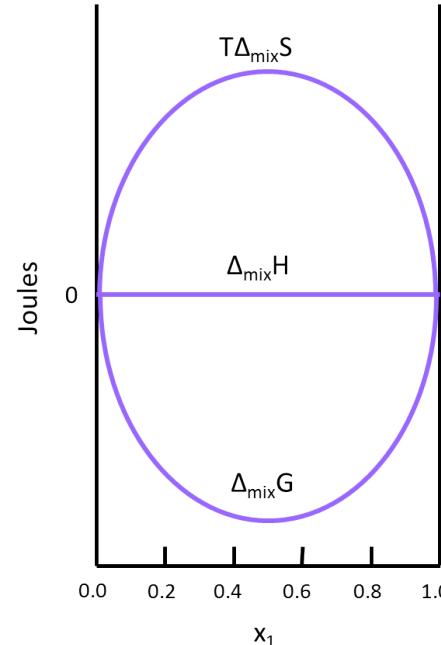
Boltzmann law for the entropy of mixing:

$$\Delta S_M = k \ln \Omega$$

$k$  : Boltzmann's constant

$\Omega$  : Number of possible arrangements  
in space that a molecule may assume

$$\Omega = \frac{N_0!}{N_1!N_2!}$$



With Stirling's approximation for large  $N$ :  
 $\ln N! \approx N \ln N - N$

$$\Delta S_m = -k[N_1 \ln n_1 + N_2 \ln n_2]$$

$N_1, N_2$ : numbers of molecules 1 and 2  
 $n_1, n_2$ : mole fractions

Components forming an ideal solution will be always be completely miscible

# Entropy of Mixing

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$$\Delta S_m = -k[N_1 \ln n_1 + N_2 \ln n_2]$$

There are 3 important features to this expression:

1.  $n_1$  and  $n_2$  are always between 0 and 1 in a mixture.  
Logarithm term  $<0, \Delta S_m > 0$ , favors spontaneous mixing
2. Equal molecular size
3. All configurations were equally probable, no energetic benefit or price for having 1 next to 1 and 2 next to 2, versus having 1 next to 2

# Entropy of Mixing

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$$\Delta S_m = -k[N_1 \ln n_1 + N_2 \ln n_2]$$

Here  $n_1$  and  $n_2$  are mole fraction !!

Change to volume fraction:

$$N_1 = \frac{N_0 \nu_1}{n_1}$$

$N_1$ : number of molecules 1

$n_1$ : number of lattice site occupied by molecule 1

$N_0$ : total number of lattice site

$\nu_1$ : volume fraction of molecule 1 in a mixture of molecules 1 and 2

$$\nu_1 = \frac{V_1}{V_1 + V_2}$$

Entropy of mixing per lattice site:

$$\Delta S_{mix} = -k \left[ \frac{\nu_1}{n_1} \ln \nu_1 + \frac{\nu_2}{n_2} \ln \nu_2 \right]$$

## Case 2: Regular Solution ( $\Delta H_M \neq 0$ )

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### small molecule mixture

Concept introduced by Hildebrand: molecules in solution interact in some way, but the possible arrangements of the molecules on the lattice do not change

→ Combinatorial entropy  $\Delta S_M$  is the same like the ideal case

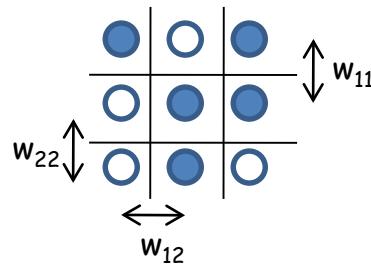
**Assumption:** no volume change on mixing  
no interactions strong enough to produce clustering

→

$\Delta G_M$  = ideal  $(-T\Delta S_M)$  plus an **enthalpy term**

# Enthalpy of Mixing $\Delta H_M$ – Interaction Parameter $\chi$

$w_{11}$  and  $w_{22}$  **interaction energies** which act between two molecules of type 1, or 2 respectively,  
All molecules attract one another by dispersion forces, so  $w_{11}$  and  $w_{22}$  are negative.  
 $w_{12}$  interaction energy between molecules 1 and 2 (is also negative).



**exchange energy**  $\Delta w = w_{12} - \frac{1}{2} w_{11} - \frac{1}{2} w_{22}$

$\Delta w \geq 0$  (like prefers like)

$z$  = coordination number,

the number of nearest neighbor for a lattice

Total number of such contacts:  $xN_2zv_1 = N_1v_2z$

( $x$  = degree of polymerization, small molecules  $x = 1$ )

$$\Delta H_M = N_1 v_2 z \Delta w$$

$$\chi \equiv \frac{z \Delta w}{kT}$$

**interaction parameter**, exchange energy per molecule, normalized by the thermal energy  $kT$

$$\rightarrow \Delta H_M = k T N_1 v_2 \chi$$

$$\Delta G_M = kT(\chi_1 N_1 v_2 + N_1 \ln v_1 + N_2 \ln v_2)$$

Enthalpic term

Entropic term

when  $\chi > 0$ ,  $\Delta H_M > 0$   
Opposes spontaneous mixing

$\Delta S_M > 0$  favor mixing

## Dilute Solution of Polymer: Flory- Huggins Theory

$$\Delta G_M = kT(\underbrace{\chi_1 N_1 v_2}_{\text{Enthalpic term}} + \underbrace{N_1 \ln v_1 + N_2 \ln v_2}_{\text{Entropic term}})$$

## Flory Huggins model special case of regular solution theory:

## Polymer – Solvent System

$$v_1 = \frac{N_1}{N_1 + xN_2} \quad v_2 = \frac{xN_2}{N_1 + xN_2}$$

using volume fraction

The difference to the regular solution theory is  $x$  = degree of polymerization, which reduces the polymer contribution to the entropy of mixing

$$\chi = \beta_1 + \frac{V_1}{RT} (\delta_1 - \delta_2)^2$$

Related to the solubility parameter  
with  $V_1$  = lattice size volume = solvent size

# Flory – Huggins Parameter $\chi$

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According to the value of  $\chi$ , we have three different kinds of behavior:

1.  $\chi < \frac{1}{2}$ : the polymer chain is expanded. This is referred to as **good solvent** behavior
2.  $\chi = \frac{1}{2}$  :the repulsive effect of excluded volume is exactly cancelled by the attractive effect of the polymer/solvent interactions. The chain is an ideal random walk. This situation is known as the **theta condition**.
3.  $\chi > \frac{1}{2}$  :the effect of the polymer/solvent interaction outweighs the repulsive excluded volume interaction, and the chain collapse to form a compact globule. This is referred to as a **poor solvent** behavior.

# Summary: Entropy of Mixing

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## Small molecule mixtures:

$$\Delta S_m = -k[N_1 \ln n_1 + N_2 \ln n_2]$$

$N_1, N_2$ : numbers of molecules 1 and 2  
 $n_1, n_2$ : mole fractions

## Polymer solvent mixtures:

$$\Delta S_m = -k[N_1 \ln v_1 + N_2 \ln v_2]$$

$N_1, N_2$ : numbers of molecules 1 (solvent) and 2 (polymer)

$v_1, v_2$ : volume fractions

$x$ : degree of polymerization

$$v_1 = \frac{N_1}{N_1 + xN_2} \quad v_2 = \frac{xN_2}{N_1 + xN_2}$$

## Polymer polymer mixtures:

$$\Delta S_m = -k[N_1 \ln v_1 + N_2 \ln v_2]$$

$N_1, N_2$ : numbers of molecules 1 and 2

$v_1, v_2$ : volume fractions

$x_1, x_2$ : degree of polymerization

$$v_1 = \frac{x_1 N_1}{x_1 N_1 + x_2 N_2} \quad v_2 = \frac{x_2 N_2}{x_1 N_1 + x_2 N_2}$$

# Summary

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1. An expression for the free energy of mixing based on the Flory-Huggins theory is developed. This is a mean-field theory and reduces to the standard regular solution theory when the degree of polymerization of the polymer component is set equal to 1. The numerous assumption of the model were identified.
2. The concept of a theta solvent emerges as a central feature of polymer solutions. It has 4 equivalent operational definitions:
  - (a) the temperature where  $A_2 = 0$
  - (b) **the temperature where the interaction parameter  $\chi = 1/2$**
  - (c) the temperature at which an infinite molecular weight fraction would just precipitate  
(the limit of the critical temperature  $T_c$  as  $M \rightarrow \infty$ )
  - (d) a solvent in which  $R_g \sim M^{1/2}$Physically, a theta solvent is one in which the polymer-solvent interactions are rather unfavorable, so that the chain shrinks to its random-walk dimensions. This contraction cancels the effect of the excluded volume interactions, which otherwise swell the chain to self-avoiding conformations:  $R_g \sim M^{3/5}$
3. The Flory Huggins parameter can be related to thermodynamic quantities such as the heat of vaporization and the cohesive energy density.