Lecture

Polymer Thermodynamics

0331 L 337

6. Thermodynamics of Polymer Solutions
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.1. Introduction

\[ x_A^F n^F = x_A^I n^I + x_A^II n^II \quad n^F = n^I + n^II \]

\[ x_A^F (n^I + n^II) = x_A^I n^I + x_A^II n^II \rightarrow \frac{x_A^F - x_A^I}{x_A^II - x_A^I} = \frac{n^I}{n^II} \]
Polymer Thermodynamics
6. Thermodynamics of Polymer Solutions
6.1. Introduction

Phase equilibrium conditions

\[
\begin{align*}
\mu_A^{L1} &= \mu_A^{L2} \\
\mu_B^{L1} &= \mu_B^{L2} \\
P^{L1} &= P^{L2} = P
\end{align*}
\]

Instability limit

\[
\left( \frac{\partial^2 \Delta_{\text{MIX}}}{\partial x^2} g(x) \right) = 0
\]

critical conditions

\[
\left( \frac{\partial^3 \Delta_{\text{MIX}}}{\partial x^3} g(x) \right) = 0
\]

T, P=constant
Polymer Thermodynamics
6. Thermodynamics of Polymer Solutions

6.1. Introduction

\[ \mu_i(T, P, x_i) = \mu_{0i}(T, P) + RT \ln x_i + RT \ln \gamma_i \]

\[ \mu_{0L1}(T, P) + RT \ln x_{A_L1} + RT \ln \gamma_{A_L1} = \mu_{0L2}(T, P) + RT \ln x_{A_L2} + RT \ln \gamma_{A_L2} \]

\[ \ln x_{A_L1} + \ln \gamma_{A_L1} = \ln x_{A_L2} + \ln \gamma_{A_L2} \rightarrow \ln \left( x_{A_L1} \gamma_{A_L1} \right) = \ln \left( x_{A_L2} \gamma_{A_L2} \right) \]

\[ x_{A_L1} \gamma_{A_L1} = x_{A_L2} \gamma_{A_L2} \]

g\textsuperscript{E}-model for the determination of the activity coefficients is necessary

i.e.

\[ \frac{g^E}{RT} = A(T)x_Ax_B = A(T)x_A \left( 1 - x_A \right) \]

\[ \ln \gamma_B = A(T)x_A^2 \]

\[ \ln \gamma_A = A(T)x_B^2 \]
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6.1. Introduction

\[
\ln\left(\frac{x_{B}^{L1}}{x_{B}^{L2}}\right) = A(T) \left[ 2\left( x_{B}^{L1} - x_{B}^{L2} \right) + \left( x_{B}^{L2} \right)^{2} \left( x_{B}^{L1} \right)^{2} \right]
\]

\[
\ln\left(\frac{x_{A}^{L1}}{x_{A}^{L2}}\right) = A(T) \left[ 2\left( x_{A}^{L1} - x_{A}^{L2} \right) + \left( x_{A}^{L2} \right)^{2} \left( x_{A}^{L1} \right)^{2} \right]
\]

system of equations made from 2 equations → 2 quantities can be calculated

3 possibilities:

1) \( T \) and \( x_{A}^{L1} \rightarrow \) fixed \( x_{A}^{L2} \)
2) \( T \) and \( x_{A}^{L2} \rightarrow \) fixed \( x_{A}^{L1} \)
3) \( x_{A}^{L1} \) and \( x_{A}^{L2} \rightarrow \) fixed \( T \)
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.1. Introduction

Spinodale

\[
\left( \frac{\partial^2 \Delta_{\text{MIX}} g(x)}{\partial x^2} \right) = 0 \quad \ln \gamma_B = A(T)x_A^2 \quad \ln \gamma_A = A(T)x_B^2
\]

\[
\Delta_{\text{MIX}} g = RT \left( x_A \ln x_A + x_B \ln x_B + x_A \ln \gamma_A + x_B \ln \gamma_B \right)
\]

\[
\left( \frac{\partial^2 \Delta_{\text{MIX}} g}{\partial x_A^2} \right) = \left( \frac{1}{x_A} + \frac{1}{1 - x_A} - 2A(T) \left( 1 - x_A \right) - 2A(T)x_A \right) = \frac{1}{x_A} + \frac{1}{1 - x_A} - 2A(T) = 0
\]

Critical point

\[
\left( \frac{\partial^3 \Delta_{\text{MIX}} g(x)}{\partial x^3} \right) = - \frac{1}{x_A^2} + \frac{1}{\left( 1 - x_A \right)^2} = 0 \rightarrow x_A^C = \frac{1}{2}
\]

\[A_C(T) = 2 \quad A(T) > A_C(T) \Rightarrow \text{spontaneous demixing}\]

\[A(T) < A_C(T) \Rightarrow \text{stable or metastable}\]
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.1. Introduction

Problems:

1. Why are polymers usually do not dissolve in normal solvent?
2. Do we have phase separation (LLE) for polymer solutions?
3. How depends phase separation on the molecular weight?

Differences between low-molecular weight mixtures and polymer solution

<table>
<thead>
<tr>
<th>low-molecular weight mixture</th>
<th>polymer solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>i.e. benzene + toluene</td>
<td>i.e. PS in cyclohexane</td>
</tr>
<tr>
<td>both components have approximately the same size</td>
<td>both components show a big difference in size</td>
</tr>
<tr>
<td>the structure of both components do not depend on concentration</td>
<td>structure of polymer depends on solvent concentration</td>
</tr>
<tr>
<td></td>
<td>→ additional parameter molecular weight distribution</td>
</tr>
</tbody>
</table>
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.1. Introduction

Taking into account the differences in size:

\[ r_i = \frac{L_i}{L_{\text{standard}}} \]

\( L_{\text{standard}} \) = property of an arbitrarily chosen standard segment (i.e. solvent or monomer unit)

Properties

1. possibility \( L = \text{molar volume} \)
   disadvantage: volumes depend on temperature
2. possibility \( L = \text{molar mass} \)
3. possibility \( L = \text{degree of polymerization} \)
4. possibility \( L = \text{van der Waals-volume (quantity } b \text{ in the van der Waals – equation of state)} \)
   advantage: available by experiments using X-ray diffraction or by prediction from molecular data (group-contribution method by Bondi)
   do not depend on temperature
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.1. Introduction

Taking into account the differences in size:

- **division of polymers into segments**
- **segment-related thermodynamic quantities** (segment-molare quantities)

Polymer solution made from solvent (A) + polymer (B)

\[
x_A = \frac{r_A x_A}{r_A x_A + r_B x_B}
\]

\[
z = \frac{r_A z_A + r_B z_B}{r_A x_A + r_B x_B}
\]

i.e. cyclohexane + polystyrene  \(M_{PS}=100000\text{g/mol} \quad x_B=0.00001\)

\(L_{\text{standard}}= \text{molar mass of solvent} = 84.16\text{g/mol}\)

\[
r_{PS} = \frac{100000\text{ g/mol}}{84.16\text{ g/mol}} = 1188.2
\]

\[
r_{CH} = \frac{84.16\text{ g/mol}}{84.16\text{ g/mol}} = 1
\]

\[
x_{PS} = \frac{1188.2 \ast 0.00001}{1 \ast (1-0.00001)+1188.2 \ast 0.00001} = 0.01174
\]
6. Thermodynamics of Polymer Solutions

6.1. Introduction

The structure of polymer depends on concentration.

- **Diluted polymer solution**: No entanglements of the polymer chain.
  - Concentration $c < c^\star$

- **Semi-diluted polymer solution, entanglements of the polymer chain**: Overlapping concentration $c = c^\star$
  - Concentration $c = c^\star$

- **Semi-diluted polymer solution, entanglements of the polymer chain**: Overlapping concentration $c^\star$
  - Concentration $c > c^\star$
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.1. Introduction

vapor pressure of polymer solution

Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.1. Introduction

Phase diagram
cyclohexane + PS
at different molecular weights
in [kg/mol] of PS

Example: $M_{PS}=37000$ g/mol
$w_{PS}=0.1$, $T=280$ K

Experimental result: demixing

$$\left( \frac{\partial^2 \Delta_{mix} g}{RT} \right) \frac{\partial^2}{\partial x_{PS}^2} > 0 \quad \text{(meta)stable}$$
$$\left( \frac{\partial^2 \Delta_{mix} g}{RT} \right) \frac{\partial^2}{\partial x_{PS}^2} = 0 \quad \text{spinodale}$$
$$\left( \frac{\partial^2 \Delta_{mix} g}{RT} \right) \frac{\partial^2}{\partial x_{PS}^2} < \quad \text{instable}$$
6. Thermodynamics of Polymer Solutions

6.1. Introduction

real low-molecular weight mixture

\[ WW_{AB} \neq WW_{AA} \neq WW_{BB} \]

model of regular mixture

Hildebrand (1933)

The real behavior can be explained completely by enthalpic effects.

\[ s^E = 0 \rightarrow g^E = h^E \]

\[ WW_{AB} = \sqrt{WW_{AA} WW_{BB}} \]

derivations from the behavior of an ideal mixture are caused by intermolecular interaction
6. Thermodynamics of Polymer Solutions

6.1. Introduction

Hildebrand model of regular mixture

The real behavior can be explained completely by enthalpic effects.

\[ S^E = 0 \Rightarrow g^E = h^E \]

\[ \frac{g^E}{RT} = v\phi_A\phi_B D_{AB} \]

\[ \phi_i = \frac{x_i v_{0i}}{\sum_{i=1}^{k} x_i v_{0i}} \]

\[ v^E = 0 \Rightarrow v = \sum_{i=1}^{k} x_i v_{i0} = \sum_{i=1}^{k} x_i v_i \]

\[ \delta_i \text{ solubility parameter} \]

\[ \delta_{CH} = 16.7 \text{ (J/cm}^3\text{)}^{1/2} \quad \delta_{PS} = 17.4 \text{ (J/cm}^3\text{)}^{1/2} \]

\[ D_{CHPS} = \frac{(16.7 - 17.4)^2 \text{ JmolK}}{cm^3 8.314J 280K} = 0.00021 \text{ mol/cm}^3 \]
Hildebrand model of regular mixture
The real behavior can be explained completely by enthalpic effects.

\[
\frac{g^E}{RT} = \nu \phi_A \phi_B D_{AB} \\
D_{CHPS} = 0.00021 \frac{\text{mol}}{\text{cm}^3}
\]

\[
\left( \frac{\partial^2 \Delta_{Mix}g}{\partial x_B^2} \right) = \frac{1}{1 - x_B} + \frac{1}{x_B} - \frac{2D_{AB}v_{0A}^2v_{0B}^2}{v^3} < 0
\]

Table book:

\[
\nu_{CH} = 111 \frac{\text{cm}^3}{\text{mol}} \quad \rho_{PS} = 1.0556 \frac{\text{g}}{\text{cm}^3}
\]

\[
\nu_{PS} = \frac{M_{PS}}{\rho_{PS}} = \frac{37000 \text{g cm}^3}{\text{mol} 1.0556 \text{g}} = 35051 \frac{\text{cm}^3}{\text{mol}}
\]

\[
v = x_{CH} \nu_{CH} + x_{PS} \nu_{PS}
\]
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.1. Introduction

example: \( M_{PS} = 37000 \text{ g/mol} \), \( w_{PS} = 0.1 \), \( T = 280 \text{ K} \)

\[
D_{CHPS} = 0.00021 \frac{\text{mol}}{\text{cm}^3} \quad \nu_{CH} = 111 \frac{\text{cm}^3}{\text{mol}} \quad \nu_{PS} = 35051 \frac{\text{cm}^3}{\text{mol}}
\]

\[
\left( \frac{\partial^2 \Delta_{Mix} g / RT}{\partial x_{PS}^2} \right) = \frac{1}{1 - x_{PS}} + \frac{1}{x_{PS}} - \frac{2D_{CHPS} \nu_{CH}^2 \nu_{PS}^2}{\nu^3} < 0
\]

\[
x_{PS} = \frac{n_{PS}}{n_{PS} + n_{CH}} = \frac{m_{PS}}{M_{PS}} + \frac{m_{CH}}{M_{CH}} = \frac{w_{PS} m}{M_{PS}} + \frac{w_{CH} m}{M_{CH}} = \frac{w_{PS}}{M_{PS}} + \frac{w_{CH}}{M_{CH}}
\]

\[
x_{PS} = 0.00025267 \quad \nu = 119.828 \frac{\text{cm}^3}{\text{mol}} \quad \left( \frac{\partial^2 \Delta_{Mix} g / RT}{\partial x_{PS}^2} \right) = 263.65
\]

interaction are not the reasons for the strong real effects

cancel to experimental findings
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.2. Flory-Huggins Theory

model of ideal-a thermic mixture
→ Flory-Huggins mixture

J.P. Flory (1930)
M.L. Huggins

The real behavior can be explained completely by entropic effects.

\[ h^E = 0 \rightarrow g^E = -Ts^E \]

\[ WW_{AB} = WW_{AA} = WW_{BB} \]
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.2. Flory-Huggins Theory

Model of ideal-athermic mixture

\[ h^E = 0 \rightarrow g^E = -T s^E \]

\[ \text{WW}_{AB} = \text{WW}_{AA} = \text{WW}_{BB} \]

Polymer chains will be arranged on lattice sites of equal sizes (i.e. \( v_{0A} \)).
The number of occupied lattice site depends on segment number \( r \).

Boltzmann’s definition of entropy

\[ S = k_B \ln \Omega \]

\( k_B \) Boltzmann’s constant
\( \Omega \) thermodynamic probability
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.2. Flory-Huggins Theory

Statistical Interpretation of Entropy

Number of possible configurations for 3 distinguishable particles in 3 rooms

Number of possible configurations corresponds to the permutations of the number of particles:

$$P = N! = 3 \times 2 \times 1 = 6$$

Probability:

$$W = \frac{N!}{N_1! N_2! N_3! \ldots N_i!}$$

$W$ is called „thermodynamic probability“ and it is the number of possible configurations for a given macroscopic state.
6. Thermodynamics of Polymer Solutions

6.2. Flory-Huggins Theory

Example: distribution of 4 particles with identical energy in 4 volumes.

A

\[ W_A = \frac{4!}{(4!0!0!0!)} = \frac{4!}{4!} = 1 \]

B

\[ W_B = \frac{4!}{(3!0!1!0!)} = \frac{4!}{3!} = 4 \]

C

\[ W_C = \frac{4!}{(2!1!1!0!)} = \frac{4!}{2!} = 12 \]

D

\[ W_D = \frac{4!}{(1!1!1!1!)} = \frac{4!}{1!} = 24 \]

The macroscopic state D can be realized by the most configurations.

The macroscopic state D has the highest thermodynamic probability.
6. Thermodynamics of Polymer Solutions

6.2. Flory-Huggins Theory

Model of ideal-athermic mixture

\[ h^E = 0 \rightarrow g^E = -TS^E \]

\[ S = k_B \ln \Omega \]

\( \Omega \) represents the number of distinguishable possibilities of the system to fill the lattice places with particles.

size of the lattice place: \( v_{0A} \)

Every lattice place is occupied either with polymer segment or with a solvent molecule.

The polymer segments of a polymer chain are connected by chemical bond and hence they can not move freely.

\( N_A \)-solvent molecules + \( N_B \)-polymer chains (every chain consist of \( r \)-segments)

number of total lattice places: \( N_0 = N_A + r \cdot N_B \)

every lattice place is surrounded by \( q \) next neighbors (coordination number)

cubic lattice \( q = 6 \)
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.2. Flory-Huggins Theory

model of ideal-athermic mixture

\[
 h^E = 0 \rightarrow g^E = -T S^E \quad S = k_B \ln \Omega
\]

the first polymer chain has \( \nu_1 \) possibility to arrange

\[ \nu_1 = N_0 q (q - 1)^{r-2} \]

number of empty lattice places \( N_f \), if the lattice is filled with \( i-1 \) polymer chains

\[ N_f = N_0 - (i - 1) \, r \]

the probability to find an empty place is equal to \( N_f/N_0 \)

number of possibilities to arrange for the chain \( i \):

\[ \nu_i = N_f \left( \frac{N_f}{N_0} \right)^{r-1} q (q - 1)^{r-2} \]

\[ \Omega = \left[ \frac{\prod_{i=1}^{i=N_B} \nu_i}{N_B! \, 2^r} \right] \]

\[ \Delta_{\text{Mix}} S = -R \left[ \left( 1 - x_B \right) \ln(1 - x_B) + \frac{x_B}{r} \ln x_B \right] \]
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.2. Flory-Huggins Theory

Model of ideal-athermic mixture

\( \Delta_{\text{Mix}} s = -R \left[ (1-x_B) \ln(1-x_B) + \frac{x_B}{r} \ln x_B \right] \)

\( \Delta_{\text{MIX}} g = RT \left[ (1-x_B) \ln(1-x_B) + \frac{x_B}{r} \ln x_B \right] \)

\( \left( \frac{\partial \Delta_{\text{MIX}} g / RT}{\partial x_B} \right) = -\ln(1-x_B) - 1 + \frac{1}{r} \ln \left( \frac{x_B}{r} \right) + \frac{1}{r} \)

\( \left( \frac{\partial^2 \Delta_{\text{MIX}} g / RT}{\partial x_B^2} \right) = \frac{1}{1-x_B} + \frac{1}{rx_B} = 0 \rightarrow \frac{rx_B + \left(1-x_B\right)}{r \left(1-x_B\right) x_B} = 0 \rightarrow x_B = -\frac{1}{r-1} \)

Ideal-athermic mixture can not demixed

\( r \geq 1 \) negative segment mole fraction is nonsense
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.2. Flory-Huggins Theory

model of real polymer solutions

\[
\Delta_{\text{MIX}} g = RT \left[ (1-x_B) \ln(1-x_B) + \frac{x_B}{r} \ln x_B \right] + g^R
\]

description of the derivation of a real polymer solution from an ideal-athermic mixture

\[
\Delta \varepsilon = \varepsilon_{AB} - \frac{1}{2} \left[ \varepsilon_{AA} + \varepsilon_{BB} \right]
\]
interaction energy between lattice places

\[
\chi = \frac{q \Delta \varepsilon}{k_B T}
\]
Flory-Huggin‘s interaction parameter

\[
g^R = h^R = N_0 q x_B (1-x_B) \Delta \varepsilon
\]

\[
\begin{array}{|c|c|}
\hline
\chi & \text{Condition} \\
\hline
<0 & \text{good solvent} \\
=0 & \text{Ideal - athermic mixture} \\
>0 & \text{bad solvent} \\
\hline
\end{array}
\]
6. Thermodynamics of Polymer Solutions

6.2. Flory-Huggins Theory

model of real polymer solutions

\[
\Delta_{\text{MIX}} g = RT \left[ (1 - x_B) \ln(1 - x_B) + \frac{x_B}{r} \ln x_B \right] + g^R
\]

\[
\chi = \frac{q \Delta \varepsilon}{k_B T} \quad \Delta \varepsilon = \frac{k_B T \chi}{q}
\]

\[
\chi \text{ Flory-Huggins interaction parameter}
\]

\[
g^R = h^R = N_0 q x_B (1 - x_B) \Delta \varepsilon = N_0 q x_B (1 - x_B) \frac{k_B T \chi}{q} = RT x_B (1 - x_B) \chi
\]

\[
\frac{\Delta_{\text{MIX}} g}{RT} = (1 - x_B) \ln(1 - x_B) + \frac{x_B}{r} \ln x_B + x_B (1 - x_B) \chi
\]

Flory-Huggins-equation
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.2. Flory-Huggins Theory

\[
\frac{\Delta_{\text{MIX}} g}{RT} = (1 - x_B) \ln(1 - x_B) + \frac{x_B}{r} \ln x_B + x_B (1 - x_B) \chi
\]

\[
\left( \frac{\partial \Delta_{\text{MIX}} g / RT}{\partial x_B} \right) = -\ln\left(1 - x_B\right) - 1 + \frac{1}{r} \ln\left(\frac{x_B}{x_B}\right) + \frac{1}{r} + \left(1 - 2x_B\right) \chi
\]

\[
\left( \frac{\partial^2 \Delta_{\text{MIX}} g / RT}{\partial x_B^2} \right) = \frac{1}{1 - x_B} + \frac{1}{rx_B} - 2\chi = 0 \quad \text{spinodal condition}
\]

\[
\left( \frac{\partial^3 \Delta_{\text{MIX}} g / RT}{\partial x_B^3} \right) = \frac{1}{\left(1 - x_B\right)^2} - \frac{1}{r\left(x_B\right)^2} = 0 \quad \text{critical condition}
\]
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.2. Flory-Huggins Theory

\[
\frac{\Delta_{\text{MIX}} g}{RT} = (1 - x_B) \ln(1 - x_B) + \frac{x_B}{r} \ln x_B + x_B (1 - x_B) \chi
\]

\[
\left( \frac{\partial^3 \Delta_{\text{MIX}} g / RT}{\partial x_B^3} \right) = \frac{1}{(1 - x_B)^2} - \frac{1}{r(x_B)^2} = 0 \rightarrow r(x_B)^2 = \left(1 - x_B\right)^2 = 1 - 2x_B + \left(\frac{x_B}{r}\right)^2
\]

\[
0 = 1 - 2x_B + (1 - r)\left(\frac{x_B}{r}\right)^2 \rightarrow 0 = \frac{1}{1 - r} - \frac{2x_B}{(1 - r)} + \left(\frac{x_B}{r}\right)^2
\]

\[
x_{B1,2} = \frac{2}{2(1 - r)} \pm \sqrt{\frac{4}{4(1 - r)^2} - 1} = \frac{1}{1 - r} \pm \frac{1}{1 - r} \sqrt{1 - (1 - r)} = \frac{1 \pm \sqrt{r}}{1 - r}
\]

\[
0 < x_{B1,2} < 1 \rightarrow \quad x_{BC} = \frac{1 - \sqrt{r}}{1 - r} = \frac{\sqrt{r} - 1}{r - 1}
\]
6. Thermodynamics of Polymer Solutions

6.2. Flory-Huggins Theory

Flory-Huggins theory

\[
x_{Bc} = \frac{\sqrt{r - 1}}{r - 1}
\]
6. Thermodynamics of Polymer Solutions

6.2. Flory-Huggins Theory

\[ \Delta_{\text{MIX}} g = \frac{(1 - x_B) \ln(1 - x_B) + \frac{x_B}{r} \ln x_B + x_B (1 - x_B) \chi}{RT} \]

\[ x_{Bc} = \frac{1 - \sqrt{r}}{(1 - r)} \quad \text{für } r \to \infty \Rightarrow \lim_{r \to \infty} x_{Bc} = \frac{1}{2\sqrt{r}} = \frac{1}{2} = 0 \]

\[ \left( \frac{\partial^2 \Delta_{\text{MIX}} g / RT}{\partial x_B^2} \right) = \frac{1}{1 - x_B} + \frac{1}{rx_B} - 2\chi = 0 \quad \text{für } r \to \infty \Rightarrow \frac{1}{1 - x_B} = 2\chi \]

\[ x_B \to 0 \Rightarrow \chi_C = 1/2 \]

for polymers with \( r \to \infty \)

\[ \chi = 0.5 \quad \text{spinodal} \]

\[ > \quad \text{instable} \]

\[ < \quad \text{stable} \]
Flory-Huggins parameter for polymer + solvent - systems

<table>
<thead>
<tr>
<th>system</th>
<th>T [°C]</th>
<th>$\chi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>cellulose nitrate + acetone</td>
<td>25</td>
<td>0.27</td>
</tr>
<tr>
<td>polyisobutylene + benzene</td>
<td>25</td>
<td>0.5</td>
</tr>
<tr>
<td>polystyrene + toluene</td>
<td>25</td>
<td>0.44</td>
</tr>
<tr>
<td>PVC + THF</td>
<td>26</td>
<td>0.15</td>
</tr>
<tr>
<td>rubber + CCl$_4$</td>
<td>20</td>
<td>0.28</td>
</tr>
<tr>
<td>rubber + benzene</td>
<td>25</td>
<td>0.44</td>
</tr>
<tr>
<td>rubber + acetone</td>
<td>25</td>
<td>1.37</td>
</tr>
</tbody>
</table>
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.2. Flory-Huggins Theory

\( \chi \) can also depend on polymer concentration and molecular weight.

\( \chi \) can also depend on polymer concentration and molecular weight.

Values of CH/PVME:
- M_w [kg/mol]: 81, 51, 28

T = 65°C

B. A. Wolf, University of Mainz, 1995
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.2. Flory-Huggins Theory

\[ \chi \]

$T = 35^\circ C$

$T = 45^\circ C$

$T = 55^\circ C$

B. A. Wolf, University of Mainz, 1995
formal division of $\chi$ in an enthalpic- and an entropic part

$$\chi = \chi_H + \chi_S = \frac{(h_\chi - Ts_\chi)}{RT} = \frac{h_\chi}{RT} - \frac{s_\chi}{R}$$

$$\chi_S = - \frac{s_\chi}{R} \left( \frac{\partial \chi}{\partial T} \right) = - \frac{h_\chi}{RT^2} \rightarrow h_\chi = -RT^2 \left( \frac{\partial \chi}{\partial T} \right)$$

$$\chi_H = \frac{h_\chi}{RT} = \frac{-RT^2 \left( \frac{\partial \chi}{\partial T} \right)}{RT} = -T \left( \frac{\partial \chi}{\partial T} \right)$$

special case: $-\chi_H = \chi_S \Rightarrow \chi = 0$

pseudo-ideal state = Theta-state

$$\chi = \chi_H + \chi_S = \frac{h_\chi}{RT} - \frac{s_\chi}{R} = \frac{1}{R} \left( \frac{h_\chi}{T} - s_\chi \right) \Rightarrow \frac{h_\chi}{T} = s_\chi$$

Theta-temperature
Flory-Huggins parameter for PMMA + solvent systems

<table>
<thead>
<tr>
<th>solvent</th>
<th>$\chi$</th>
<th>$\chi_H$</th>
<th>$\chi_S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>chloroform</td>
<td>0.36</td>
<td>-0.08</td>
<td>0.44</td>
</tr>
<tr>
<td>benzene</td>
<td>0.43</td>
<td>-0.02</td>
<td>0.45</td>
</tr>
<tr>
<td>dioxane</td>
<td>0.43</td>
<td>0.04</td>
<td>0.39</td>
</tr>
<tr>
<td>THF</td>
<td>0.45</td>
<td>0.03</td>
<td>0.42</td>
</tr>
<tr>
<td>toluene</td>
<td>0.45</td>
<td>0.03</td>
<td>0.42</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.48</td>
<td>0.03</td>
<td>0.45</td>
</tr>
<tr>
<td>m-xylene</td>
<td>0.51</td>
<td>0.2</td>
<td>0.31</td>
</tr>
</tbody>
</table>

entropic effects are more important than enthalpic effects
6. Thermodynamics of Polymer Solutions

6.2. Flory-Huggins Theory

\[ \chi \]

TL/PDMS 170
T = 35°C

\[ \chi_H \]

\[ \chi_S \]

B. A. Wolf, Universität Mainz, 1995
Prediction of $\chi$

Cohesive Energy $e_{Coh}$: internal energy of the material if all of its intermolecular forces are eliminated

$$e_{Coh} = \frac{F^2}{v(298K)}$$

F molar attraction constant
v molar volume

Solubility parameter $\delta$

$$\delta = \sqrt{\frac{e_{coh}}{v}} \quad \delta \left[ \frac{J^{1/2}}{mol^{3/2}} \right]$$

Solubility of polymer P in solvent S

$$\frac{h^R}{RT} = x_B (1 - x_B) \chi \approx x_B (1 - x_B) \left[ \frac{(\delta_B - \delta_A)^2}{vRT} \right] \rightarrow \chi = \frac{(\delta_B - \delta_A)^2}{vRT}$$
Prediction of $\chi$ example: solubility of polystyrene at 25°C

First step: Calculation of atomic indices $\delta$ and valence atomic $\delta^V$

Second step: Calculation of connectivity indices

$$\beta_{ij} = \delta_i \delta_j \quad \beta^V_{ij} = \delta^V_i \delta^V_j$$

$$\chi^0 \equiv \sum_{\text{vertices}} \frac{1}{\sqrt{\delta}} \quad \chi^V \equiv \sum_{\text{vertices}} \frac{1}{\sqrt{\delta^V}} \quad \chi^1 \equiv \sum_{\text{edges}} \frac{1}{\sqrt{\beta}} \quad \chi^V \equiv \sum_{\text{edges}} \frac{1}{\sqrt{\beta^V}}$$

$$\chi^0 = 5.3973 \quad \chi^V = 4.6712 \quad \chi^1 = 3.9663 \quad \chi^V = 3.0159$$
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.2. Flory-Huggins Theory

Prediction of $\chi$ example: solubility of polystyrene at 25°C

Fourth step: Calculation of molar volume

$$\nu = \nu_W \left( 1.42 + 0.15 \left( \frac{T}{T_g} \right) \right)$$

$$T_g = 373.15 \text{K}$$

$$\nu_W = \left( 3.861803^0 \chi + 13.748435^1 \chi^V \right) \frac{cm^3}{mol}$$

$$= \left( 3.861803 \times 5.3973 + 13.748435 \times 3.0159 \right) \frac{cm^3}{mol} = 62.31 \frac{cm^3}{mol}$$

$$\nu = 62.31 \frac{cm^3}{mol} \left( 1.42 + 0.15 \left( \frac{298K}{373K} \right) \right) = 95.95 \frac{cm^3}{mol}$$
6. Thermodynamics of Polymer Solutions

6.2. Flory-Huggins Theory

Prediction of $\chi$ example: solubility of polystyrene at 25°C

Third step: Calculation of molar attraction constant $F$

$$F = \left[ 97.95 \left( -0\chi + 2\left( 0\chi^V + 1\chi + 1\chi^V \right) \right) \right] \frac{\sqrt{Jcm^3}}{mol^2} + 134.61 \left( N_{Si} - N_{Br} - N_{Cyc} \right)$$

$$F = \left[ 97.95 \left( -5.3973 + 2\left( 4.6712 + 3.9663 + 3.0159 \right) \right) \right] \frac{\sqrt{Jcm^3}}{mol^2} + 134.61 \left( 0 - 0 - 0 \right)$$

$$F = 1754.2 \frac{\sqrt{Jcm^3}}{mol^2}$$
Prediction of $\chi$ example: solubility of polystyrene

Fifth step: Calculation cohesive energy $e_{\text{Coh}}$

$$e_{\text{Coh}} = \frac{F^2}{\nu(298 K)}$$

$$F = 1754.2 \sqrt{\frac{\text{Jcm}^3}{\text{mol}^2}} \quad \nu = 95.95 \frac{\text{cm}^3}{\text{mol}}$$

$$e_{\text{Coh}} = \frac{(1754.2)^2 \text{Jcm}^3 \text{mol}}{\text{mol}^2 95.95 \text{cm}^3} = 32.07 \frac{\text{kJ}}{\text{mol}}$$

Sixth step: Calculation of solubility parameter $\delta$

$$\delta = \sqrt{\frac{e_{\text{coh}}}{\nu}} = \sqrt{\frac{32.07 \text{kJmol}}{\text{mol} 95.95 \text{cm}^3}} = 18.28 \sqrt{\frac{\text{J}}{\text{cm}^3}}$$
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.2. Flory-Huggins Theory

Prediction of $\chi$ example: solubility of polystyrene

Seventh step: Calculation of interaction parameter $\chi$

$$\chi = \frac{(\delta_B - \delta_A)^2}{vRT}$$

<table>
<thead>
<tr>
<th>solvent</th>
<th>$\delta_A$ [J/cm³]</th>
<th>$\chi$</th>
<th>solvent quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-hexane</td>
<td>14,86</td>
<td>0,4520</td>
<td>middle</td>
</tr>
<tr>
<td>toluene</td>
<td>18,17</td>
<td>0,0005</td>
<td>excellent</td>
</tr>
<tr>
<td>benzene</td>
<td>18,56</td>
<td>0,0030</td>
<td>excellent</td>
</tr>
<tr>
<td>dioxane</td>
<td>20,42</td>
<td>0,1769</td>
<td>good</td>
</tr>
<tr>
<td>methanol</td>
<td>29,60</td>
<td>4,9669</td>
<td>poor-LLE</td>
</tr>
</tbody>
</table>
6. Thermodynamics of Polymer Solutions

6.2. Flory-Huggins Theory

Application of Flory-Huggins Theory to LLE phase equilibrium conditions

low molecular weight mixtures

\[
\begin{align*}
\mu_A^{L1} &= \mu_A^{L2} \\
\mu_B^{L1} &= \mu_B^{L2} \\
P^{L1} &= P^{L2} = P
\end{align*}
\]

\[
\mu_B = \left( \frac{\partial G}{\partial n_B} \right)_{T,P,n_A} 
\rightarrow G = G_{0A} + G_{0B} + \Delta_{MIX} G = n_A g_{0A} + n_B g_{0B} + n \Delta_{MIX} g
\]

\[
\frac{\Delta_{MIX} g}{RT} = \left(1 - x_B \right) \ln \left(1 - x_B \right) + \frac{x_B}{r} \ln x_B + x_B \left(1 - x_B \right) \chi
\]
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.2. Flory-Huggins Theory

Application of Flory-Huggins Theory to LLE

$$G = n_A g_{0A} + n_B g_{0B} + RT n \left[ (1-x_B) \ln(1-x_B) + \frac{x_B}{r} \ln x_B + x_B (1-x_B) \chi \right]$$

$$\mu_A = \left( \frac{\partial G}{\partial n_A} \right)_{T,P,n_B} = g_{0A} + RT \left( \ln \left( \frac{x_A}{x_A} \right) + x_B \left( 1 - \frac{1}{r} \right) + \left( \frac{x_B}{x_B} \right)^2 \chi \right)$$

$$\mu_A / RT = \mu_{0A} / RT + \ln \left( \frac{x_A}{x_A} \right) + x_B \left( 1 - \frac{1}{r} \right) + \left( \frac{x_B}{x_B} \right)^2 \chi$$

$$\mu_B = \left( \frac{\partial G}{\partial n_B} \right)_{T,P,n_A} = g_{0B} + RT \left[ \frac{1}{r} \ln \left( \frac{x_B}{x_B} \right) - x_A \left( 1 - \frac{1}{r} \right) + \left( \frac{x_A}{x_A} \right)^2 \chi \right]$$

$$\mu_B / RT = \mu_{0B} / RT + \frac{1}{r} \ln \left( \frac{x_B}{x_B} \right) - x_A \left( 1 - \frac{1}{r} \right) + \left( \frac{x_A}{x_A} \right)^2 \chi$$
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.2. Flory-Huggins Theory

Application of Flory-Huggins Theory to LLE

\[
\mu_A^{L1} \left( \frac{1}{RT} \right) + \ln \left( \frac{x_A^{L1}}{x_B^{L1}} \right) + x_B^{L1} \left( 1 - \frac{1}{r} \right) + \left( x_B^{L1} \right)^2 \chi = \mu_B^{L1} \left( \frac{1}{RT} \right) + \ln \left( \frac{x_A^{L1}}{x_B^{L1}} \right) + x_B^{L1} \left( 1 - \frac{1}{r} \right) + \left( x_B^{L1} \right)^2 \chi
\]

\[
\rightarrow \ln \left( \frac{x_A^{L1}}{x_B^{L2}} \right) = \left( x_B^{L2} - x_B^{L1} \right) \left( 1 - \frac{1}{r} \right) + \chi \left( \left( x_B^{L2} \right)^2 - \left( x_B^{L1} \right)^2 \right) \quad \text{equation 1}
\]

\[
\mu_B^{L2} \left( \frac{1}{RT} \right) + \frac{1}{r} \ln \left( \frac{x_B^{L2}}{x_A^{L2}} \right) - x_A^{L2} \left( 1 - \frac{1}{r} \right) + \left( x_A^{L2} \right)^2 \chi = \mu_B^{L2} \left( \frac{1}{RT} \right) + \frac{1}{r} \ln \left( \frac{x_B^{L2}}{x_A^{L2}} \right) - x_A^{L2} \left( 1 - \frac{1}{r} \right) + \left( x_A^{L2} \right)^2 \chi
\]

\[
\rightarrow \frac{1}{r} \ln \left( \frac{x_B^{L1}}{x_B^{L2}} \right) = \left( x_A^{L1} - x_A^{L2} \right) \left( 1 - \frac{1}{r} \right) + \chi \left( \left( x_A^{L2} \right)^2 - \left( x_A^{L1} \right)^2 \right) \quad \text{equation 2}
\]

2 equations and 3 unknowns → select one concentration in one phase
→ calculation of the concentration in the other phase and the parameter \( \chi \) using both equations, where a numerical procedure must be applied or reduce the system of equations to one equation
Application of Flory-Huggins Theory to LLE

reduce the system of equations to one equation → rearrangement of both equations according \( \chi \) → to equate both results

\[
\ln \left( \frac{\overline{x}_A^{L_1}}{\overline{x}_A^{L_2}} \right) - \left( \frac{\overline{x}_B^{L_2} - \overline{x}_B^{L_1}}{\overline{x}_B^{L_1}} \right) \left( 1 - \frac{1}{r} \right) = \frac{1}{r} \left( \frac{\overline{x}_B^{L_1}}{\overline{x}_B^{L_2}} \right) - \left( \frac{\overline{x}_A^{L_1} - \overline{x}_A^{L_2}}{\overline{x}_A^{L_2}} \right) \left( 1 - \frac{1}{r} \right)
\]

equation 3

(from equation 1)

(from equation 2)

Now: solve equation 3 in order to calculate the unknown concentration using root-searching method, like Newton-Procedure

calculate \( \chi \) using equation 1 or equation 2
6. Thermodynamics of Polymer Solutions

6.2. Flory-Huggins Theory

Application of Flory-Huggins Theory to LLE

\[ \chi(T) = \beta_1 + \frac{\beta_2}{T} + \frac{\beta_3}{T^2} \]

special cases:
- \( \beta_3 = 0 \): only one critical point can be calculated
  - \( \beta_2 > 0 \): UCST
  - \( \beta_2 < 0 \): LCST
- \( \beta_3 \neq 0 \): two critical points can be calculated
  closed miscibility gap or UCST+LCST
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.2. Flory-Huggins Theory

\[ \chi(T) = 1.186 - \frac{207.87}{T} \]

MW = 500 kg/mol

PAA + Dioxan

\[ T / °C \]

\[ w_{PAA} [%] \]
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.2. Flory-Huggins Theory

vapor pressure of polymer solutions

liquid mixture (A+B) $\leftrightarrow$ pure vapor phase (A)

solvent A + solute B

$P_B^{VL} \approx 0$

equilibrium condition:

$$d \mu_A^L(T, P, x_A) = d \mu_A^V(T, P)$$

$T = \text{constant}$

$$\frac{P^{VL}}{P_{0A}^{VL}} = \frac{a_A \phi_A^V}{\phi_A} = \frac{x_A^L \gamma_A^L \phi_A^V}{\phi_A}$$

with $\phi_A^V = \phi_A^V = 1$

$P^{VL} = x_A^L \gamma_A^L = \alpha_A^L$
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.2. Flory-Huggins Theory

vapor pressure of polymer solutions

application to polymer solution

\[
\frac{P_{VL}^A}{P_{0A}^{VL}} = a_A^L
\]

low-molecular weight mixtures

\[
\mu_i(T, P, x_i) = \mu_{0i}(T, P) + RT \ln a_i
\]

solvent in polymer solution

\[
\mu_A = \mu_{0A} + RT \left[ \ln \left( \frac{\bar{\rho}_A}{\bar{\rho}} \right) + \bar{x}_B \left( 1 - \frac{1}{r} \right) + \left( \bar{x}_B \right)^2 \chi \right]
\]

\[
\ln \left( \frac{\bar{\rho}_A}{\bar{\rho}} \right) = \ln \left( \frac{\bar{\rho}_A}{\bar{\rho}} \right) + \bar{x}_B \left( 1 - \frac{1}{r} \right) + \left( \bar{x}_B \right)^2 \chi
\]

\[
\ln \left( \frac{P_{VL}^A}{P_{0A}^{VL}} \right) = \ln \left( \frac{\bar{\rho}_A}{\bar{\rho}} \right) + \bar{x}_B \left( 1 - \frac{1}{r} \right) + \left( \bar{x}_B \right)^2 \chi
\]

possibility to determine \( \chi \) from experimental data, like vapor pressure of polymer solutions
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.2. Flory-Huggins Theory

vapor pressure of polymer solutions

liquid mixture (A+B) ↔ pure vapor phase (A)

solvent A + solute B

P_B^{VL} \approx 0

equilibria condition:

\[ d \mu_A^L(T, P, x_A) = d \mu_A^V(T, P) \]

T = constant

\[
\frac{P^{VL}}{P_{0A}^{VL}} = \frac{a_A \phi_A^V}{\phi_A} = \frac{x_A^L \gamma_A^L \phi_A^V}{\phi_A^V} = \frac{x_A^L \gamma_A^L \phi_A^V}{\phi_A}
\]

with \( \phi_A = 1 \) (ideal gas)

\[
\rightarrow \frac{P^{VL}}{P_{0A}^{VL}} = x_A^L \gamma_A^L = a_A^L
\]

Flory-Huggins theory

\[
\ln \left( \frac{P^{VL}}{P_{0A}^{VL}} \right) = \ln \left( x_A \right) + x_B \left( 1 - \frac{1}{r} \right) + \left( x_B \right)^2 \chi
\]
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.2. Flory-Huggins Theory

vapor pressure of polymer solutions

\[ P^v \] [kPa]

segment mole fraction of PS

T = 298K

- \( r=1 \chi=0 \) ideal mixture
- \( r=100 \chi=0 \) ideal-athermic mixture
- \( r=100 \chi=0.452 \) real mixture

\text{PS + n-hexane}
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.2. Flory-Huggins Theory

measurement of $\chi$: inverse gas chromatography (IGC)

IGC refers to the characterization of the chromatographic stationary phase (polymer) using a known amount of mobile phase (solvent).
The stationary phase is prepared by coating an inert support with polymer and packing the coated particles into a conventional gas chromatography column.
The activity of the given solvent can be related to its retention time on the column.

$\rightarrow$ infinity dilution regarding to the solvent

experimental information:

$V^N = V^R - V^G$

$V_0^N$ net retention volume extrapolated to zero column pressure

\[ k_0 = \frac{n_A^L V_G^G}{V^L n_A^G} = \frac{V_0^N}{V^L} \]

at infinity dilution:

\[ a_A^\infty = \left( \frac{\gamma_A}{x_A} \right)^\infty = \left( \frac{x_A P}{x_A} \right)^\infty = \left( R T n_A^L \right)^\infty \]

$V^R$ retention volume [m$^3$]

$V^G$ gas holdup [m$^3$]

$V^N$ net retention volume [m$^3$]

fugacity coefficient $= 1$
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.2. Flory-Huggins Theory

Experimental estimation of $\chi$ shows
- $\chi$ depends on temperature
- $\chi$ depends on polymer concentration
- $\chi$ depends on molecular weight

\[ \chi(T) = \beta_1 + \frac{\beta_2}{T} + \frac{\beta_3}{T^2} \]

More complex models are needed
Flory-Krigbaum Model (1950): a diluted polymer solution is considered as a dispersion of clouds consisting of polymer segments surrounded by regions of pure solvent

\[
\ln \left( a_A \right) = \ln \left( x_A \right) + x_B \left( 1 - \frac{1}{r'} \right) + \left( \kappa_1 - \psi_1 \right) \left( x_B \right)^2
\]

enthalpic parameter \quad \text{entropic parameter}

\[
\theta = \frac{\kappa_1 T}{\psi_1} \quad \theta = \text{Theta - Temperature}
\]

Difficulty: the interaction parameter depends not on concentration
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.3. Extensions of Flory-Huggins Theory

\[ g^R = RT \bar{x}_B (1 - \bar{x}_B) \chi(\bar{x}_B, T) \]

1. Possibility:
\[ \chi(\bar{x}_B, T) = \chi_0(T) + \chi_1(T)\bar{x}_B + \chi_2(T)\left(\bar{x}_B\right)^2 + \ldots + \]

advantage: very flexible
disadvantage: empirical, a lot of parameters

2. Possibility:
\[ \chi(\bar{x}_B, T) = \frac{\beta(T)}{1 - \gamma \bar{x}_B} \]

Koningsveld-Kleintjens-Eq.

advantage: very flexible, semi-empirical
   easy parameter fitting procedure using the critical point
6. Thermodynamics of Polymer Solutions

6.3. Extensions of Flory-Huggins Theory

\[ \chi \left( x_B, T \right) = \frac{\beta(T)}{1 - \gamma x_B} \]

\( \gamma = 0.32281 \)
\( \beta_1 = 0.24844 \)
\( \beta_2 = 143.307 / \text{K} \)
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.3. Extensions of Flory-Huggins Theory


high-pressure production of PE

equation of state is necessary
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.3. Extensions of Flory-Huggins Theory

Flory-Equation of State

Starting point: partition function

\[ Z = Z_{comb} \left( g v^* \right)^{rnc} \left( \tilde{v}^{1/3} - 1 \right)^{3rnc} \exp \left( \frac{rnc}{\tilde{v} T} \right) \]

combinatory factor \( Z_{comb} \)  geometrical factor \( g \)  characteristic volume \( v^* \)

\( 3rnc = \) total number of degrees of freedom ( \( r = \) segment-number, \( n = \) number of molecules, \( c = \) mean number of external degrees per segment)

\[ \tilde{v} = \frac{v}{v^*} \quad \tilde{T} = \frac{T}{T^*} \quad \tilde{P} = \frac{P}{P^*} \]

\( v^*, T^* \) and \( P^* \) are characteristic quantities = parameters of the polymer
Flory-Equation of State
Starting point: partition function

\[ Z = Z_{\text{comb}} \left( g \nu^* \right)^{rnc} \left( \tilde{\nu}^{1/3} - 1 \right)^{3rnc} \exp \left( \frac{rnc}{\tilde{\nu} T} \right) \]

from statistical thermodynamics:

\[ P = kT \left( \frac{\partial \ln Z}{\partial V} \right)_T \]

\[ \frac{\tilde{P} \tilde{\nu}}{\tilde{T}} = \frac{\tilde{\nu}^{1/3}}{\tilde{\nu}^{1/3} - 1} - \frac{1}{\tilde{T} \tilde{\nu}} \]
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.3. Extensions of Flory-Huggins Theory

Flory-Equation of State

Chemical potential for solvent:

\[ \Delta \mu_1 = RT \left[ \ln \phi_1 + \left( 1 - \frac{v_1^*}{v_2^*} \right) \phi_2 \right] + \frac{\theta_2 v_1^* X_{12}}{\tilde{v}} + v_1^* P_1^* \left[ 3 \tilde{T}_1 \ln \left( \frac{\tilde{v}_1^{1/3}}{\tilde{v}^{1/3} - 1} \right) + \frac{1}{\tilde{v}_1} - \frac{1}{\tilde{v}} \right] \]

Flory-Huggins term

Interaction term

Free volume term

Chemical potential for polymer:

\[ \Delta \mu_2 = RT \left[ \ln \phi_2 + \left( 1 - \frac{v_2^*}{v_1^*} \right) \phi_1 \right] + \frac{\theta_1^2 v_2^* X_{12}}{\tilde{v}} + v_2^* P_2^* \left[ 3 \tilde{T}_2 \ln \left( \frac{\tilde{v}_2^{1/3}}{\tilde{v}^{1/3} - 1} \right) + \frac{1}{\tilde{v}_2} - \frac{1}{\tilde{v}} \right] \]
Flory-Equation of State

calculation of the mixing volume

\[ v^E = \tilde{v} \left[ 1 - \frac{\phi_1 \tilde{v}_1 + \phi_2 \tilde{v}_2}{\tilde{v}} \right] \]

other equations of state useful in polymer thermodynamics

Sanchez-Lacombe Equation of state (SL-EOS)
lattice theory, which allows additionally empty sites

\[ \frac{\tilde{P}}{\tilde{T}} = \ln \frac{\tilde{V}}{\tilde{V} - 1} - \frac{(1 - 1/r)}{\tilde{V}} - \frac{1}{\tilde{V}^2 \tilde{T}} \]

Statistical associated fluid theory (SAFT-EOS)
takes into account additionally specific interactions like hydrogen bonding and association

Perturbed-Chain Statistical associated fluid theory (PC-SAFT-EOS)
further development of SAFT-EOS, takes the chain connectivity into account
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.3. Extensions of Flory-Huggins Theory

Polydispersity effects

three liquid phases for the system polyethylene + diphenylether at constant temperature and pressure ???

Gibbs ‘s phase rule:

\[
F = K - Ph + 2
\]

binary system: \( K=2 \) \( F=4-Ph \)
fixed \( P,T \): \( F=2 \) \( \rightarrow \) \( Ph_{\text{Max}}=2 \)

polymer solutions are not binary systems

Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.3. Extensions of Flory-Huggins Theory

Polydispersity effects
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.3. Extensions of Flory-Huggins Theory

In both phases are different polymers.

Polydispersity effects
fractionation effect

phase I
polymers with higher chain lengths

phase II
polymers with lower chain lengths

In both phases are different polymers.
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.4. Swelling Equilibria

\[
\begin{array}{cccc}
\text{solvent} & \text{polymer network} \\
& \\
\end{array}
\]

\[
\begin{array}{cccc}
T \,[^\circ\text{C}] & 20 & 30 & 40 & 50 \\
\end{array}
\]

\[
\begin{array}{cccc}
V/V_0 & 0.2 & 0.5 & 1 & 2 \\
\end{array}
\]
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.4. Swelling Equilibria

Application to drug-delivery systems
6. Thermodynamics of Polymer Solutions

6.4. Swelling Equilibria

\[ \Delta F = \Delta_{\text{MIX}} F + \Delta_{\text{el}} F = \Delta_{\text{MIX}} F + F_{\text{deformed}} - F_{\text{relaxed}} \]

\[ \Delta_{\text{el}} F \] elastic free energy (deformation of rubber, rubber elasticity)

\[ \frac{\Delta_{\text{el}} F}{RT} = C_1 \left[ \left( \frac{V}{V_0} \right)^{2/3} - 1 \right] \]

first approximation

\[ C_1 \] – fit parameter

V volume of swollen network

\( V_0 \) volume of non-swollen network

more information available:
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.5. Solid-Liquid Equilibria

starting point: \( f_i^S = f_i^L \)  
phase equilibrium condition  
iso-fugacity criteria

liquid phase: \( f_i^L = x_i^L \gamma_i^L f_{0i}^L \)  
solid phase: \( f_i^S = x_i^S \gamma_i^S f_{0i}^S \)

\[ x_i^L \gamma_i^L f_{0i}^L = x_i^S \gamma_i^S f_{0i}^S \rightarrow \frac{f_{0i}^L}{f_{0i}^S} = \frac{x_i^S \gamma_i^S}{x_i^L \gamma_i^L} \]

Calculation of pure-component properties

\[ g_{0i}^S = g_{0i}^{id}(T, P) + RT \ln \frac{f_{0i}^S}{P} \]

\[ g_{0i}^L = g_{0i}^{id}(T, P) + RT \ln \frac{f_{0i}^L}{P} \]

\[ \Delta_{LS} g_{0i} = g_{0i}^L - g_{0i}^S = RT \ln \frac{f_{0i}^L}{f_{0i}^S} \]
\[ \frac{f_{0i}^L}{f_{0i}^S} = \frac{x_i^S \gamma_i^S}{x_i^L \gamma_i^L} \]

\[ \Delta_{LS} g_{0i} = RT \ln \frac{f_{0i}^L}{f_{0i}^S} \]

\[ \Delta_{LS} g_{0i} = \Delta_{LS} h_{0i} - T \Delta_{LS} s_{0i} \]

\[ \Delta_{LS} g_{0i} = \Delta_{LS} h_{0i} - T \frac{\Delta_{LS} h_{0i}}{T_{LS}} = \Delta_{LS} h_{0i} \left(1 - \frac{T}{T_{LS}}\right) \]

\[ \ln \frac{f_{0i}^L}{f_{0i}^S} = \frac{\Delta_{LS} g_{0i}}{RT} = \frac{\Delta_{LS} h_{0i}}{RT} \left(1 - \frac{T}{T_{LS}}\right) \]

\[ \frac{\Delta_{LS} h_{0i} \left(1 - \frac{T}{T_{LS}}\right)}{RT} = \ln \left(\frac{x_i^S \gamma_i^S}{x_i^L \gamma_i^L}\right) \]

SLE for binary systems
Solids are pure-components

\[ x_i^S \gamma_i^S = 1 \]

Solid-Liquid Equilibria (SLE)

Application to polymer solution using Flory-Huggins theory

\[
\ln x_B^L = -\frac{\Delta_{LS} h_{0i}}{RT} \left( 1 - \frac{T}{T_{0i}^L} \right) - \ln \gamma_B^L
\]

\[
\ln x_A^L = -\frac{\Delta_{LS} h_{0i}}{RT} \left( 1 - \frac{T}{T_{0i}^L} \right) - \chi \left( x_A^L \right)^2
\]
Polymer Thermodynamics

6. Thermodynamics of Polymer Solutions

6.5. Solid-Liquid Equilibria

solvent
1) xylene only SLE
2) amyl acetate or nitrobenzene
   A-B SLE
   C-B LLE
   or eutectic mixture