INTRODUCTION TO

POLYMER PHYSICS:

PHASE BEHAVIOUR OF POLYMER SOLUTIONS AND BLENDS

Department of Chemical Engineering
Indian Institute of Technology Guwahati

CONTENT

Thermodynamics of Polymer Solutions:

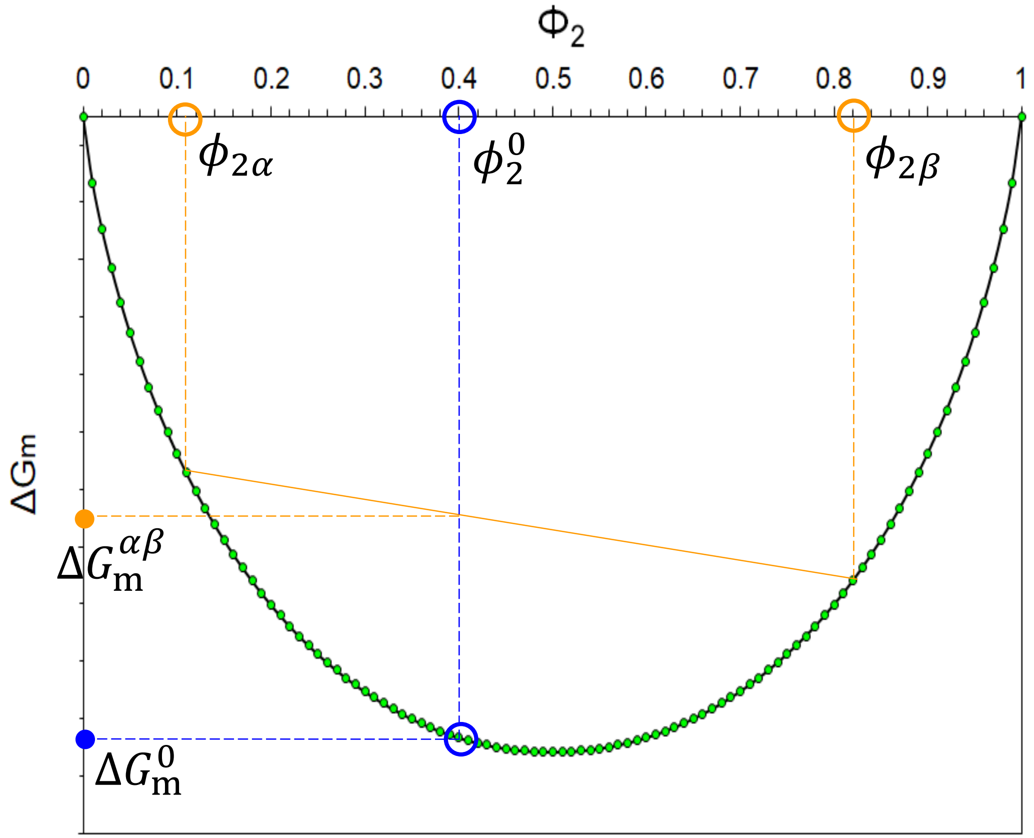
- Equilibrium and Stability
- Phase Diagram and Phase Separation
- Critical Temperature

Thermodynamics of Polymer Blends

EQUILIBRIUM AND STABILITY OF SOLUTION

EQUILIBRIUM:
The Gibbs free energy change of mixing should be negative, i.e., $\Delta G_{\mathrm{m}} < 0$.

STABILITY OF HOMOGENEOUS SOLUTION:
A plot of Gibbs free energy change of mixing versus composition should be **locally convex downwards (locally stable)**



Local stability:

$$\frac{\partial^2 \Delta G_{\mathrm{m}}}{\partial \phi_2^2} > 0$$

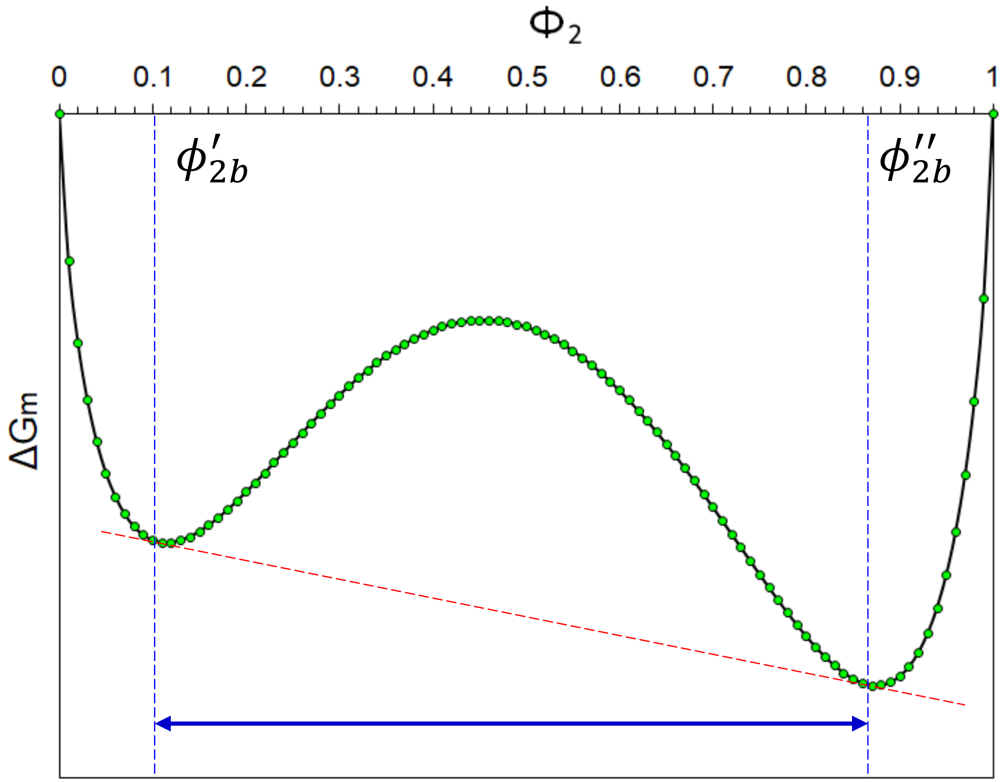
$\Delta G_{\mathrm{m}}^{0} < \Delta G_{\mathrm{m}}^{\alpha\beta}$ (for all cases)

The homogeneous solution at ϕ_2^0 is stable.

No phase separation will take place.

EQUILIBRIUM:
The Gibbs free energy change of mixing should be negative

STABILITY OF HOMOGENEOUS SOLUTION:
A plot of Gibbs free energy change of mixing versus composition should be **locally convex downwards (locally stable)**



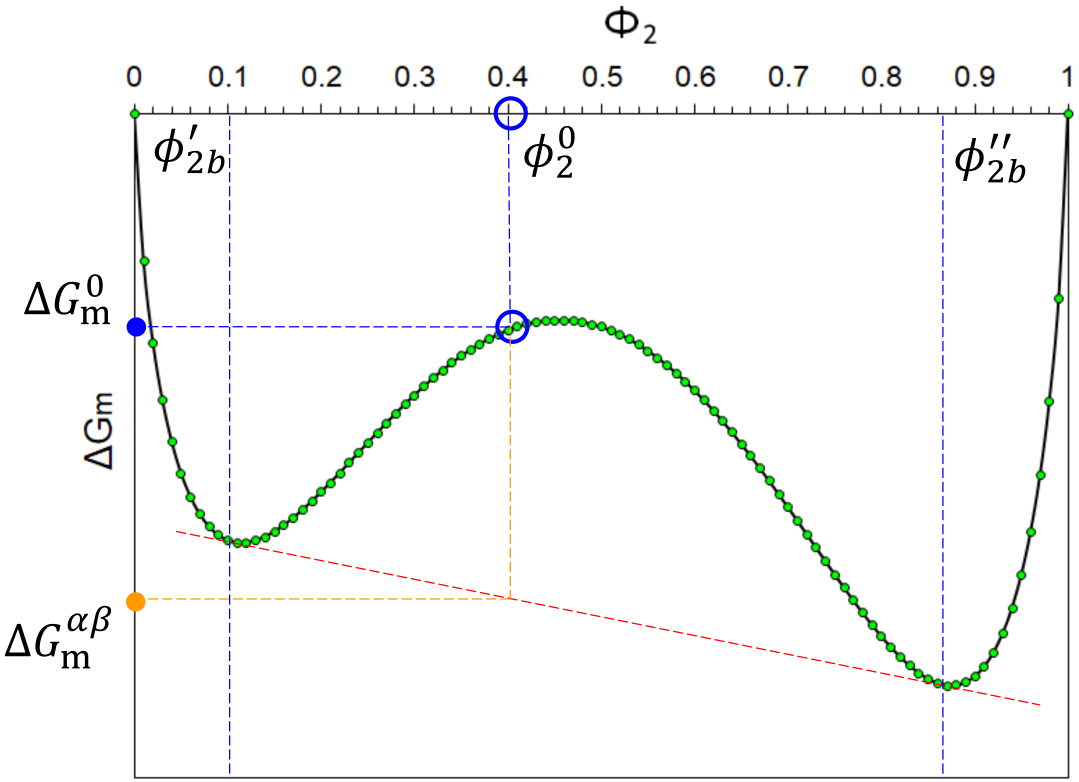
ϕ'_{2b}, ϕ''_{2b}: Binodal Points

Common Tangent Rule

Phase Separation in
$\phi'_{2b} < \phi_2 < \phi''_{2b}$
Miscibility Gap

EQUILIBRIUM:
The Gibbs free energy change of mixing should be negative

STABILITY OF HOMOGENEOUS SOLUTION:
A plot of Gibbs free energy change of mixing versus composition should be **locally convex downwards (locally stable)**



$$\Delta G_\mathrm{m}^{\alpha\beta} < \Delta G_\mathrm{m}^0$$

The homogeneous solution at ϕ_2^0 will separate into two phases having composition ϕ'_{2b} and ϕ''_{2b}.

Thermodynamics of Polymer Solutions:

Equilibrium and Stability

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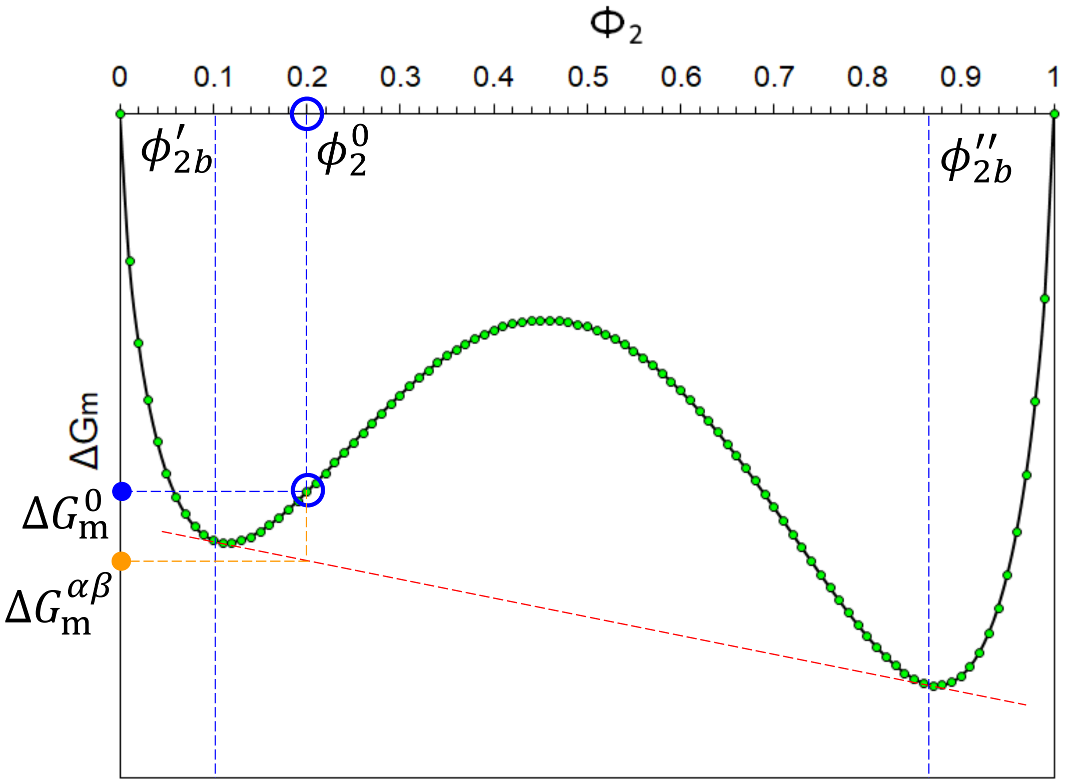
EQUILIBRIUM:
The Gibbs free energy change of mixing should be negative

STABILITY OF HOMOGENEOUS SOLUTION:
A plot of Gibbs free energy change of mixing versus composition should be **locally convex downwards (locally stable)**



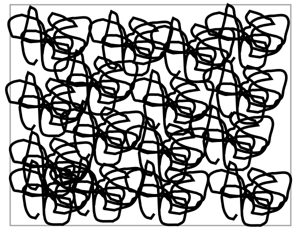
For $\phi'_{2b} < \phi_2 < \phi''_{2b}$

$$\Delta G_\mathrm{m}^{\alpha\beta} < \Delta G_\mathrm{m}^0$$

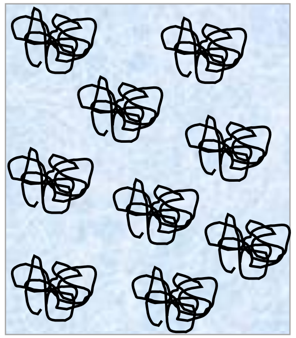
The homogeneous solution at ϕ_2^0 will separate into two phases having composition ϕ'_{2b} and ϕ''_{2b}.

EQUILIBRIUM AND STABILITY OF SOLUTION

G_1 (Solvent)



G_2 (Polymer)

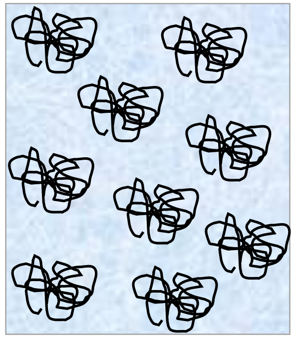


G_{12}

$(\phi_2 = \phi_2^0)$

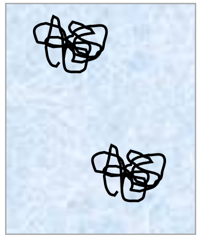
$$\Delta G_\mathrm{m}^0 = G_{12} - (G_1 + G_2) < 0$$

Phase separation into α- and β-phase will occur if $\Delta G_\mathrm{m}^{\alpha\beta} < \Delta G_\mathrm{m}^0$



$(\phi_2 = \phi_2^0)$

α-phase



$(\phi_2 = \phi_{2\alpha})$

β-phase

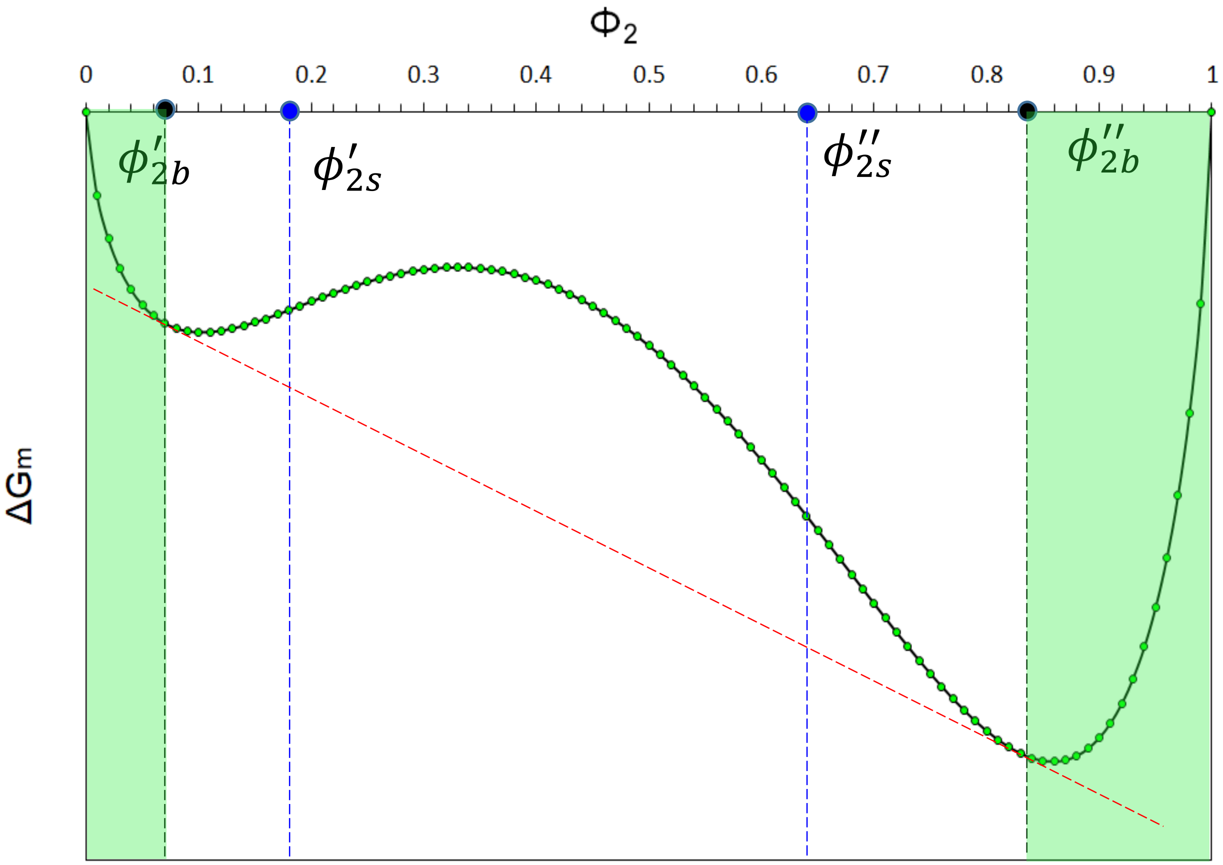
$(\phi_2 = \phi_{2\beta})$

$$\phi_2^0 = f_\alpha \phi_{2\alpha} + f_\beta \phi_{2\beta}$$

f_α: Volume fraction of α-phase

f_β: Volume fraction of β-phase

EQUILIBRIUM AND STABILITY OF SOLUTION



$0 < \phi_2 < \phi'_{2b}$ $\quad$ $\phi''_{2b} < \phi_2 < 1$

Stable, $\dfrac{\partial^2 \Delta G_\mathrm{m}}{\partial \phi_2^2} > 0$

$\phi_2 = \phi'_{2s}$ $\quad$ $\phi_2 = \phi''_{2s}$

$$\frac{\partial^2 \Delta G_\mathrm{m}}{\partial \phi_2^2} = 0$$

ϕ'_{2s}, ϕ''_{2s}: **Spinodal**

EQUILIBRIUM AND STABILITY OF SOLUTION

Thermodynamics of Polymer Solutions:

Equilibrium and Stability

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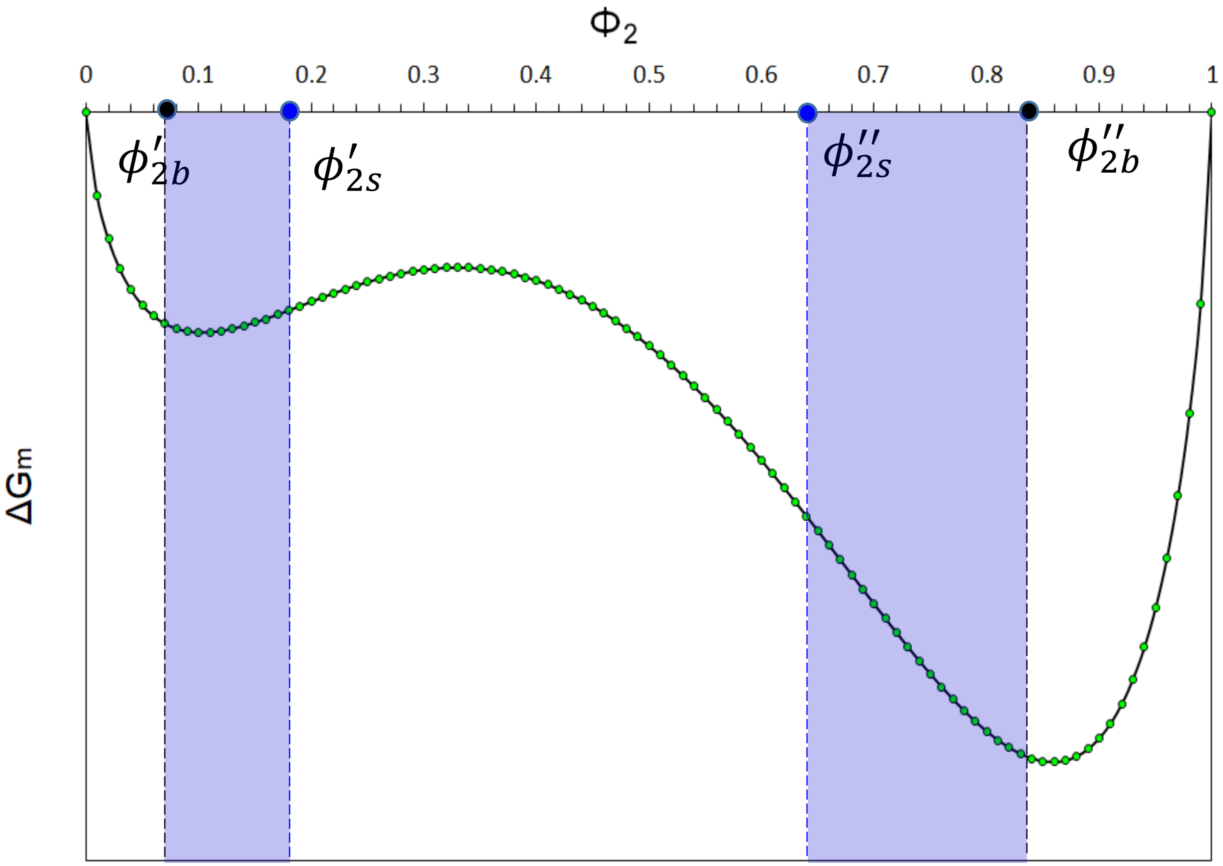


$0 < \phi_2 < \phi'_{2b}$ $\phi''_{2b} < \phi_2 < 1$

Stable, $\dfrac{\partial^2 \Delta G_\mathrm{m}}{\partial \phi_2^2} > 0$

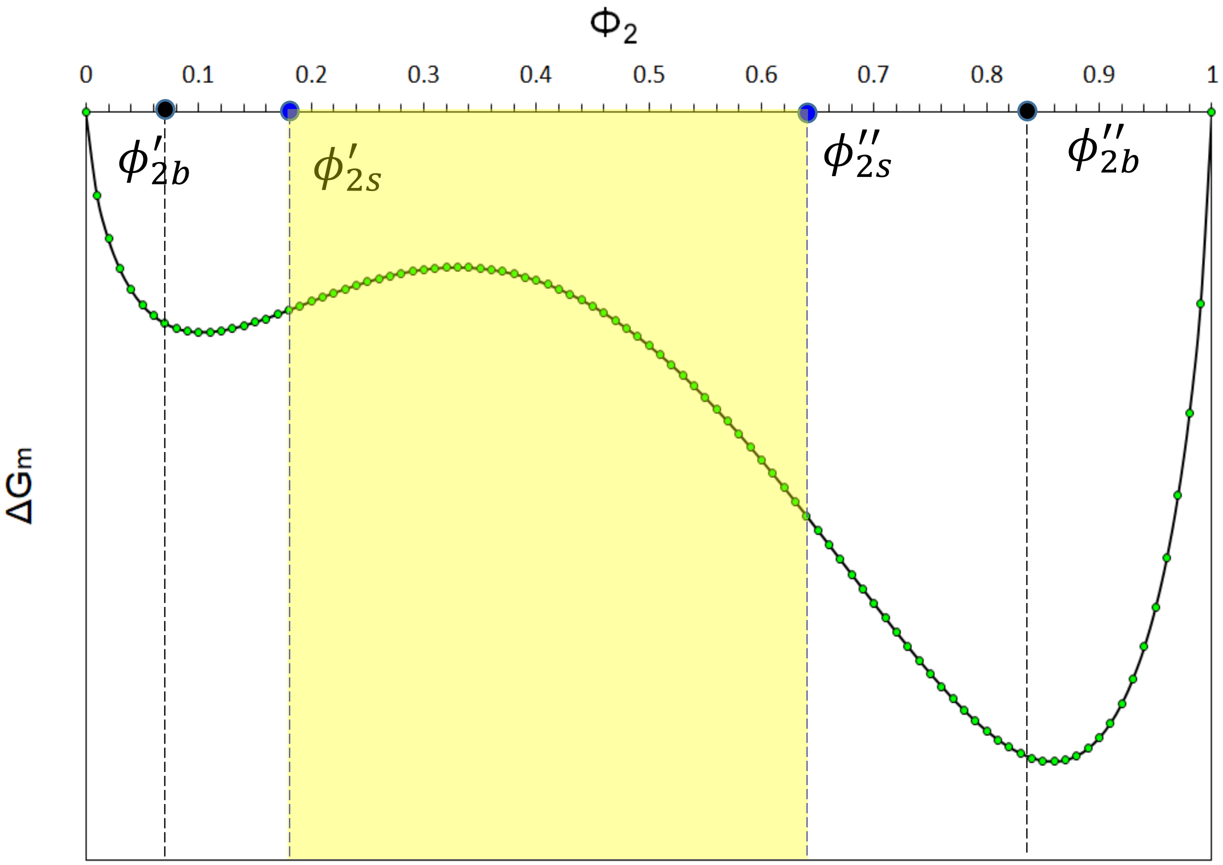
$\phi_2 = \phi'_{2s}$ $\phi_2 = \phi''_{2s}$

$$\frac{\partial^2 \Delta G_\mathrm{m}}{\partial \phi_2^2} = 0$$

$\phi'_{2b} < \phi_2 < \phi'_{2s}$ $\phi''_{2s} < \phi_2 < \phi''_{2b}$

Metastable

ϕ'_{2s}, ϕ''_{2s}: **Spinodal**



ϕ'_{2s}, ϕ''_{2s}: Spinodal

$0 < \phi_2 < \phi'_{2b}$ $\quad$ $\phi''_{2b} < \phi_2 < 1$

Stable, $\dfrac{\partial^2 \Delta G_m}{\partial \phi_2^2} > 0$

$\phi_2 = \phi'_{2s}$ $\quad$ $\phi_2 = \phi''_{2s}$

$$\frac{\partial^2 \Delta G_m}{\partial \phi_2^2} = 0$$

$\phi'_{2b} < \phi_2 < \phi'_{2s}$ $\quad$ $\phi''_{2s} < \phi_2 < \phi''_{2b}$

Metastable

$\phi'_{2s} < \phi_2 < \phi''_{2s}$

Unstable, $\dfrac{\partial^2 \Delta G_m}{\partial \phi_2^2} < 0$

EFFECT OF TEMPERATURE

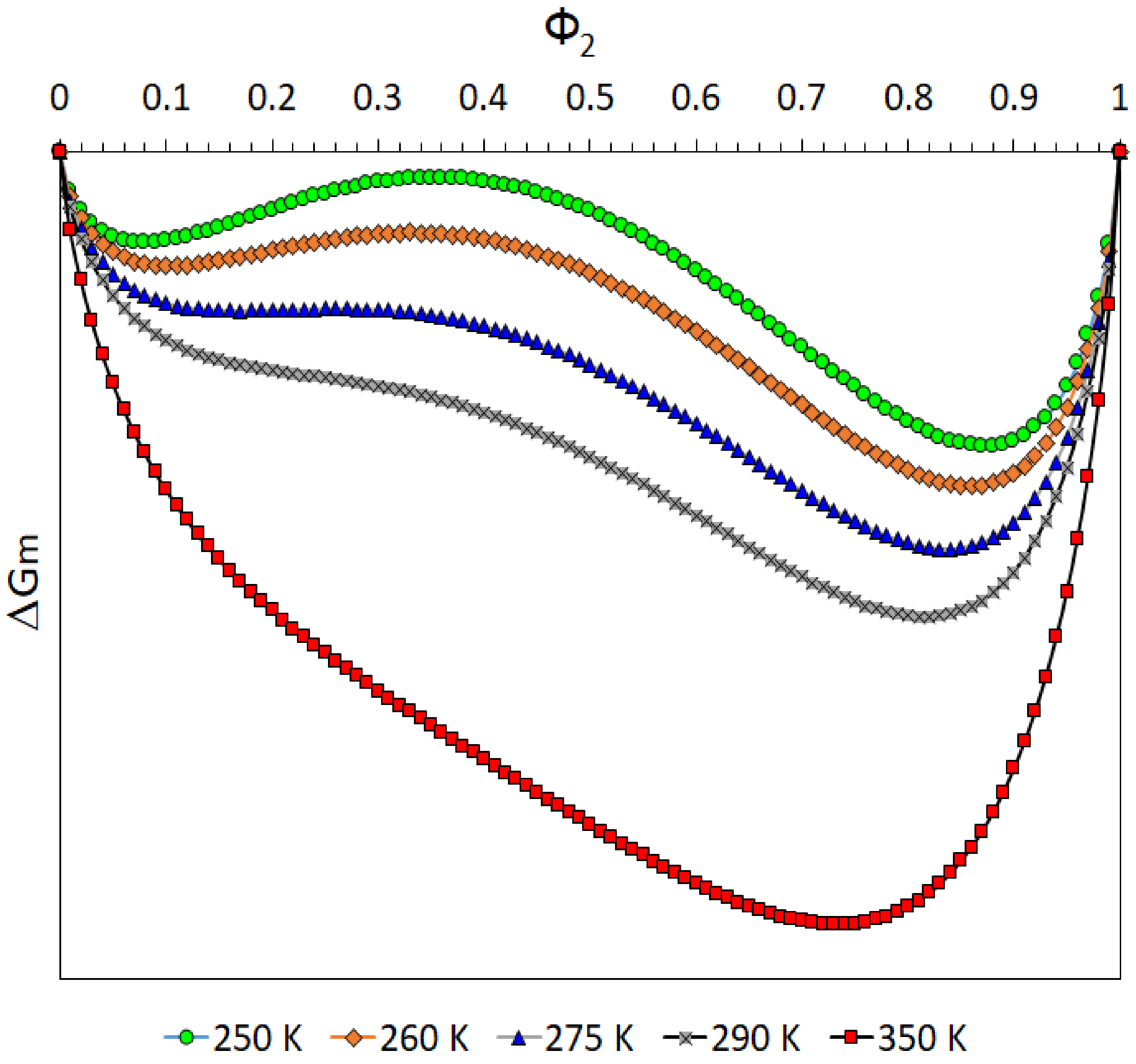
Thermodynamics of Polymer Solutions:

Equilibrium and Stability

Phase Diagram and Phase Separation

Critical Temperature

Thermodynamics of Polymer Blends



Change in temperature can change the miscibility behaviour

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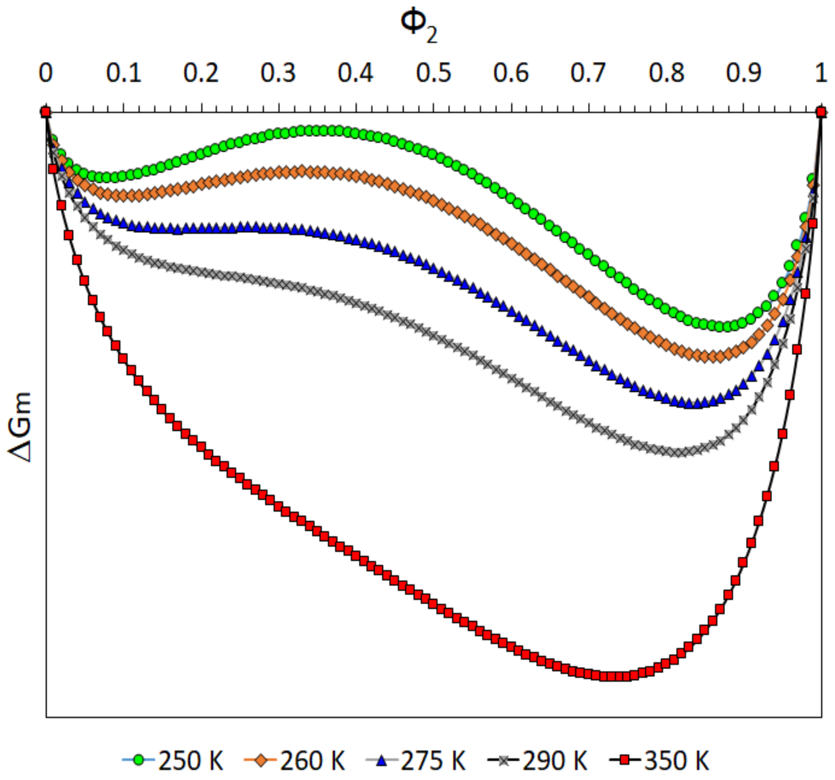

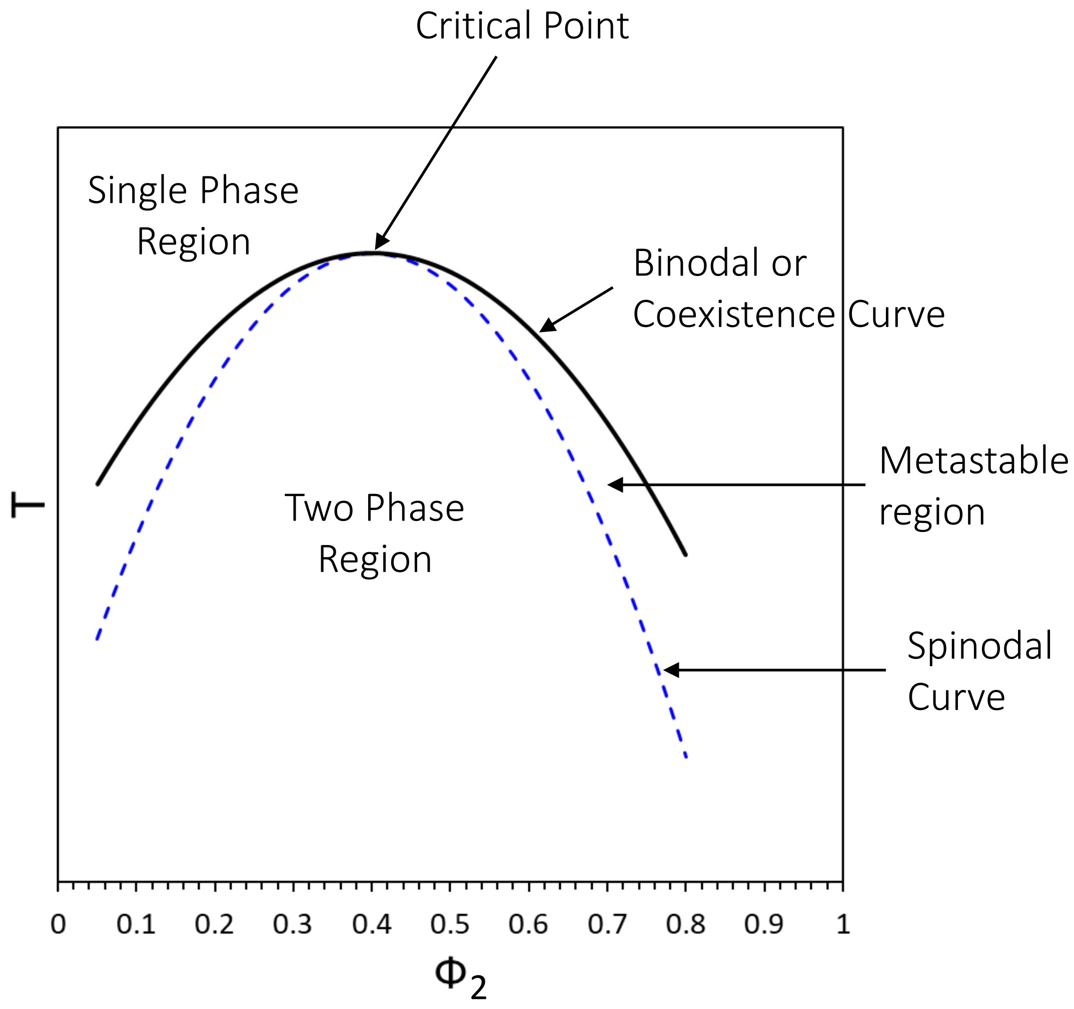

Change in temperature can change the miscibility behaviour

Flory-Huggins Equation:

$$\Delta G_{\mathrm{m}} = RT[n_1 \ln\phi_1 + n_2 \ln\phi_2 + n_1\phi_2\chi]$$

$$= k_B T[N_1 \ln\phi_1 + N_2 \ln\phi_2 + N_1\phi_2\chi]$$

$$\frac{\Delta G_{\mathrm{m}}}{N_1 + xN_2} = k_B T\left[\frac{N_1}{N_1 + xN_2}\ln\phi_1 + \frac{N_2}{N_1 + xN_2}\ln\phi_2 + \frac{N_1}{N_1 + xN_2}\phi_2\chi\right]$$

$$\overline{\Delta G}_{\mathrm{m}} = k_B T\left[\phi_1 \ln\phi_1 + \frac{\phi_2}{x}\ln\phi_2 + \phi_1\phi_2\chi\right]$$

$$\left(\overline{\Delta G}_m = \frac{\Delta G_{\mathrm{m}}}{N_1 + xN_2}\right)$$

$$\left(\phi_2 = \frac{xN_2}{N_1 + xN_2}\right)$$

$$\phi_1 = 1 - \phi_2$$

$$\boxed{\overline{\Delta G}_{\mathrm{m}} = k_B T\left[(1-\phi_2)\ln(1-\phi_2) + \frac{\phi_2}{x}\ln\phi_2 + (1-\phi_2)\phi_2\chi\right]}$$

STABILITY CONDITION

$$\overline{\Delta G}_{\mathrm{m}} = k_B T\left[(1-\phi_2)\ln(1-\phi_2) + \frac{\phi_2}{x}\ln\phi_2 + (1-\phi_2)\phi_2\chi\right]$$

$$\frac{\partial\overline{\Delta G}_{\mathrm{m}}}{\partial\phi_2} = k_B T\left[(1-\phi_2)\left[\frac{-1}{(1-\phi_2)}\right] - \ln(1-\phi_2) + \frac{\phi_2}{x}\left[\frac{1}{\phi_2}\right] + \frac{\ln\phi_2}{x} + \frac{\partial}{\partial\phi_2}\{(\phi_2-\phi_2^2)\chi\}\right]$$

$$\frac{\partial\overline{\Delta G}_{\mathrm{m}}}{\partial\phi_2} = k_B T\left[-1 - \ln(1-\phi_2) + \frac{1}{x} + \frac{\ln\phi_2}{x} + (1-2\phi_2)\chi\right]$$

$$\frac{\partial^2\overline{\Delta G}_{\mathrm{m}}}{\partial\phi_2^2} = k_B T\left[\frac{1}{(1-\phi_2)} + \frac{1}{\phi_2 x} - 2\chi\right]$$

SPINODAL CURVE

Thermodynamics of Polymer Solutions:

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Thermodynamics of Polymer Blends

Spinodal:

$$\frac{\partial^2 \overline{\Delta G_\mathrm{m}}}{\partial \phi_2^2} = 0$$

$$\frac{\partial^2 \overline{\Delta G_\mathrm{m}}}{\partial \phi_2^2} = k_B T \left[\frac{1}{(1-\phi_2)} + \frac{1}{\phi_2 x} - 2\chi \right]$$

$$k_B T \left[\frac{1}{(1-\phi_2)} + \frac{1}{\phi_2 x} - 2\chi \right] = 0$$

$$\frac{1}{(1-\phi_2)} + \frac{1}{\phi_2 x} = 2\chi$$

$$\chi_s = \frac{1}{2} \left[\frac{1}{(1-\phi_2)} + \frac{1}{\phi_2 x} \right]$$

If $\chi = a + \frac{b}{T}$

$$a + \frac{b}{T_s} = \frac{1}{2} \left[\frac{1}{(1-\phi_2)} + \frac{1}{\phi_2 x} \right]$$

$$T_s = \frac{b}{\frac{1}{2} \left[\frac{1}{(1-\phi_2)} + \frac{1}{\phi_2 x} \right] - a}$$

CRITICAL COMPOSITION

$$\left(\frac{\partial \chi_s}{\partial \phi_2}\right)_{\phi_2=\phi_{2c}} = 0$$

$$\frac{\partial \chi_s}{\partial \phi_2} = \frac{1}{2}\left[\frac{1}{(1-\phi_{2c})^2} - \frac{1}{x\phi_{2c}^2}\right] = 0$$

$$\frac{1}{(1-\phi_{2c})^2} - \frac{1}{x\phi_{2c}^2} = 0$$

$$\frac{\phi_{2c}^2}{(1-\phi_{2c})^2} = \frac{1}{x} \Longrightarrow \frac{\phi_{2c}}{(1-\phi_{2c})} = \frac{1}{\sqrt{x}}$$

$$\phi_{2c}\sqrt{x} = 1 - \phi_{2c}$$

$$\boxed{\phi_{2c} = \frac{1}{1+\sqrt{x}}}$$

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$$T_c = \frac{b}{\frac{1}{2}\left[\frac{1}{\{1-\phi_{2c}\}} + \frac{1}{x\phi_{2c}}\right] - a}$$

$$\phi_{2c} = \frac{1}{1+\sqrt{x}}$$

$$T_c = \frac{b}{\frac{1}{2}\left[\frac{1}{\left\{1-\frac{1}{1+\sqrt{x}}\right\}} + \frac{1}{\frac{x}{1+\sqrt{x}}}\right] - a}$$

$$T_c = \frac{b}{\frac{1}{2}\left[\frac{1+\sqrt{x}}{\sqrt{x}} + \frac{1+\sqrt{x}}{x}\right] - a}$$

$$T_c = \frac{b}{\frac{1+\sqrt{x}}{2\sqrt{x}}\left[1+\frac{1}{\sqrt{x}}\right] - a} = \frac{b}{\frac{\left(1+\sqrt{x}\right)^2}{2x} - a}$$

$$\chi_c = \frac{1}{2}\left[\frac{1}{\{1-\phi_{2c}\}} + \frac{1}{x\phi_{2c}}\right]$$

$$\chi_c = \frac{\left(1+\sqrt{x}\right)^2}{2x} = \frac{1}{2} + \frac{1}{\sqrt{x}} + \frac{1}{2x}$$

SPINODAL CURVE: χ_s vs ϕ_2

$$\chi_s = \frac{1}{2}\left[\frac{1}{(1-\phi_2)} + \frac{1}{\phi_2 x}\right]$$

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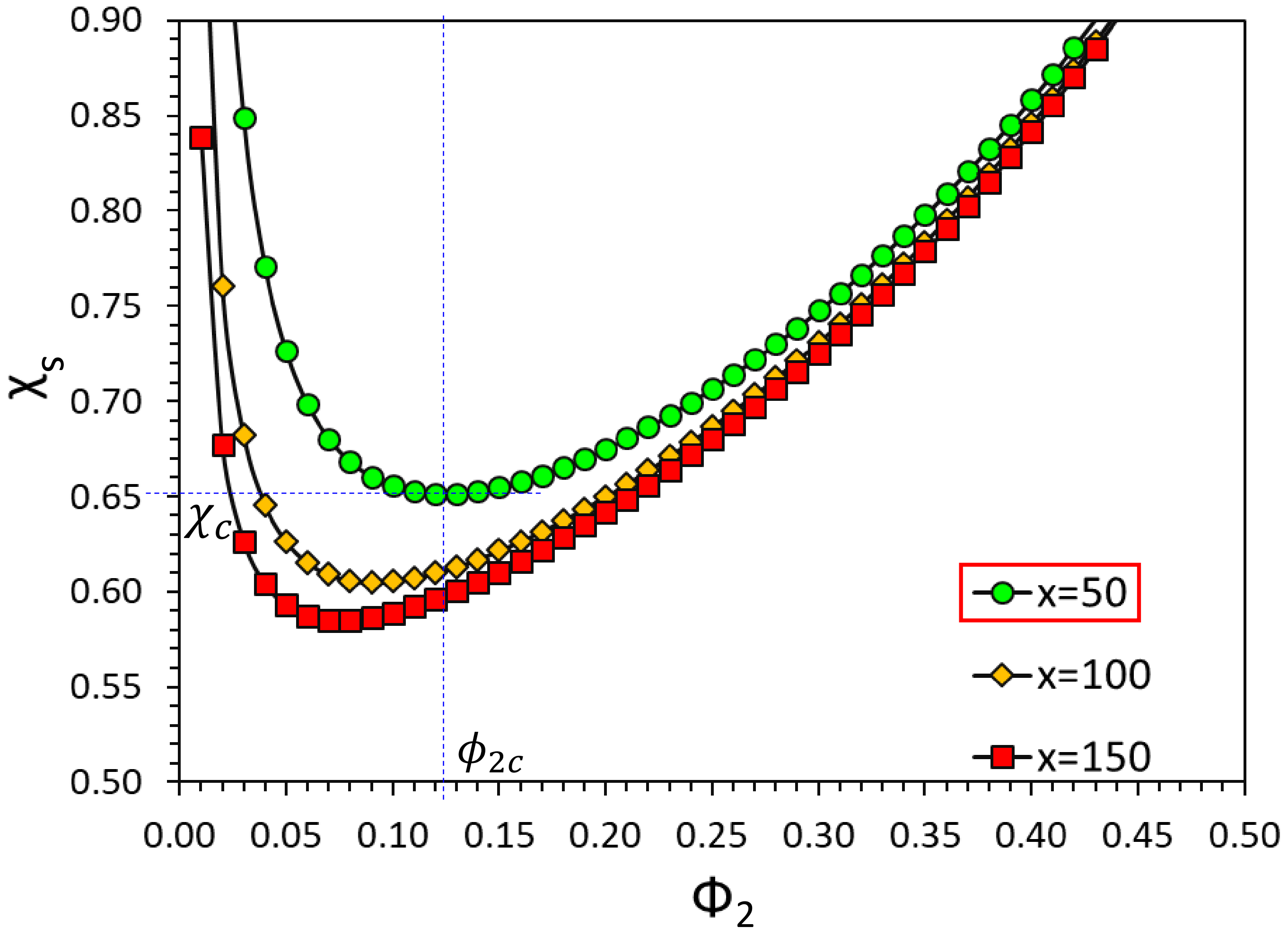

$$\phi_{2c} = \frac{1}{1+\sqrt{x}} = \frac{1}{1+\sqrt{50}} = 0.1239$$

$$\chi_c = \frac{1}{2} + \frac{1}{\sqrt{x}} + \frac{1}{2x}$$

$$= \frac{1}{2} + \frac{1}{\sqrt{50}} + \frac{1}{100} = 0.6514$$

SPINODAL CURVE: χ_s vs ϕ_2

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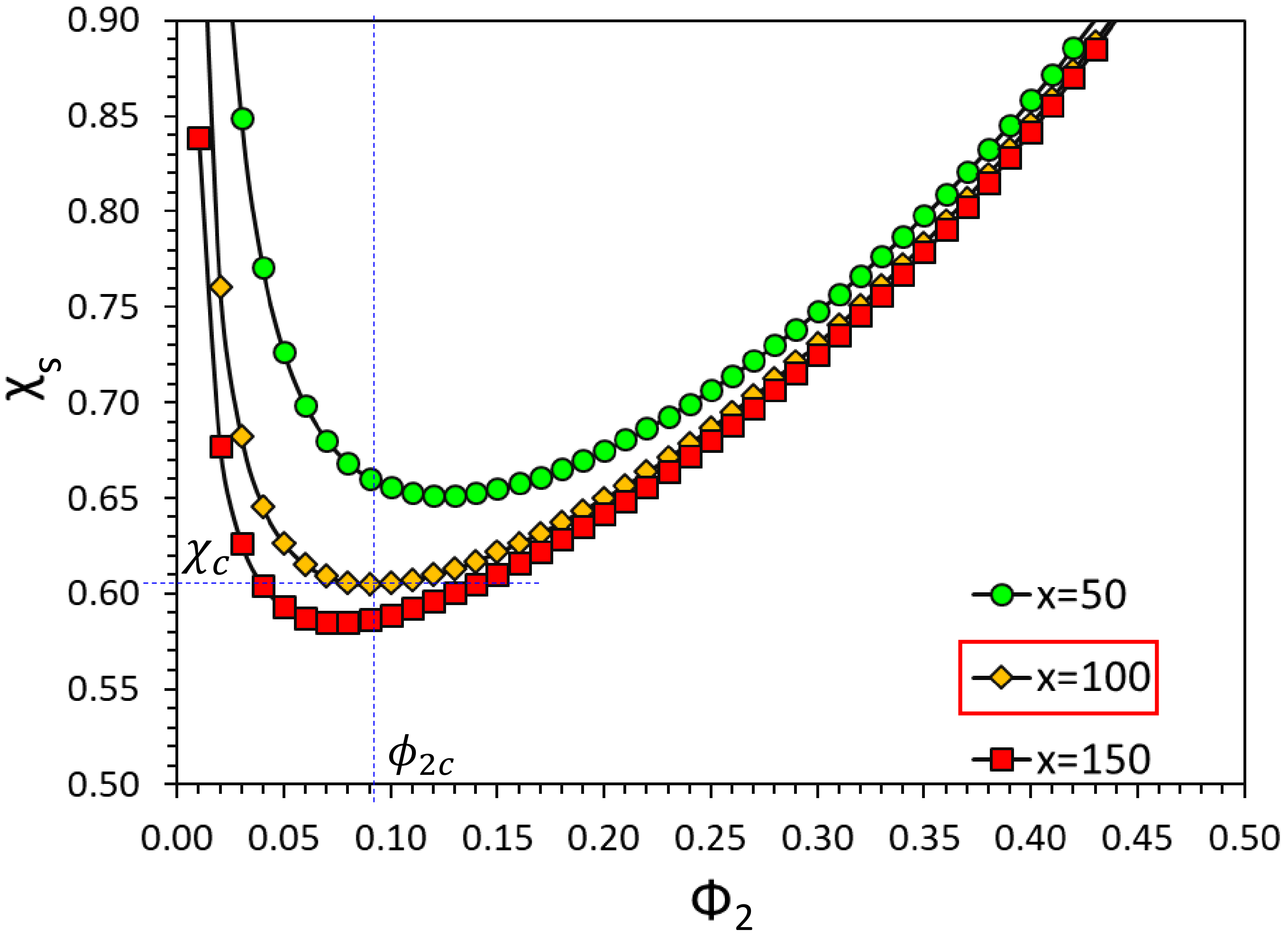
$$\chi_s = \frac{1}{2}\left[\frac{1}{(1-\phi_2)} + \frac{1}{\phi_2 x}\right]$$



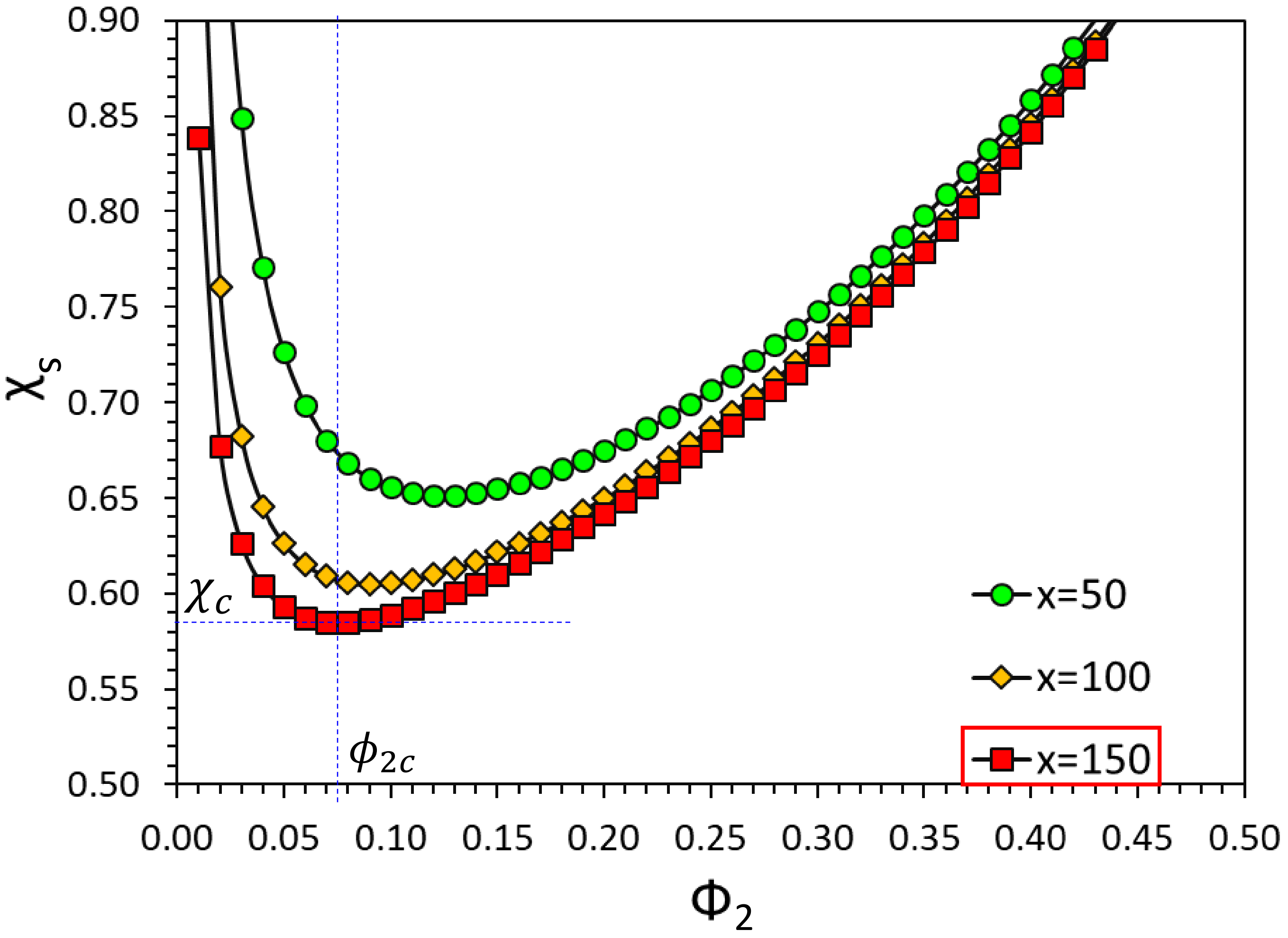
$$\phi_{2c} = \frac{1}{1+\sqrt{x}} = \frac{1}{1+\sqrt{100}} = 0.0909$$

$$\chi_c = \frac{1}{2} + \frac{1}{\sqrt{x}} + \frac{1}{2x}$$

$$= \frac{1}{2} + \frac{1}{\sqrt{100}} + \frac{1}{200} = 0.6050$$

SPINODAL CURVE: χ_s vs ϕ_2

$$\chi_s = \frac{1}{2}\left[\frac{1}{(1-\phi_2)} + \frac{1}{\phi_2 x}\right]$$



$$\phi_{2c} = \frac{1}{1+\sqrt{x}} = \frac{1}{1+\sqrt{150}} = 0.0755$$

$$\chi_c = \frac{1}{2} + \frac{1}{\sqrt{x}} + \frac{1}{2x}$$

$$= \frac{1}{2} + \frac{1}{\sqrt{150}} + \frac{1}{300} = 0.5850$$

SPINODAL CURVE: T_s vs ϕ_2

$$\chi = a + \frac{b}{T}$$

$$T_s = \frac{b}{\frac{1}{2}\left[\frac{1}{(1-\phi_2)} + \frac{1}{\phi_2 x}\right] - a}$$

$$a = 0.2, b = 125$$

Thermodynamics of Polymer Solutions:

Equilibrium and Stability

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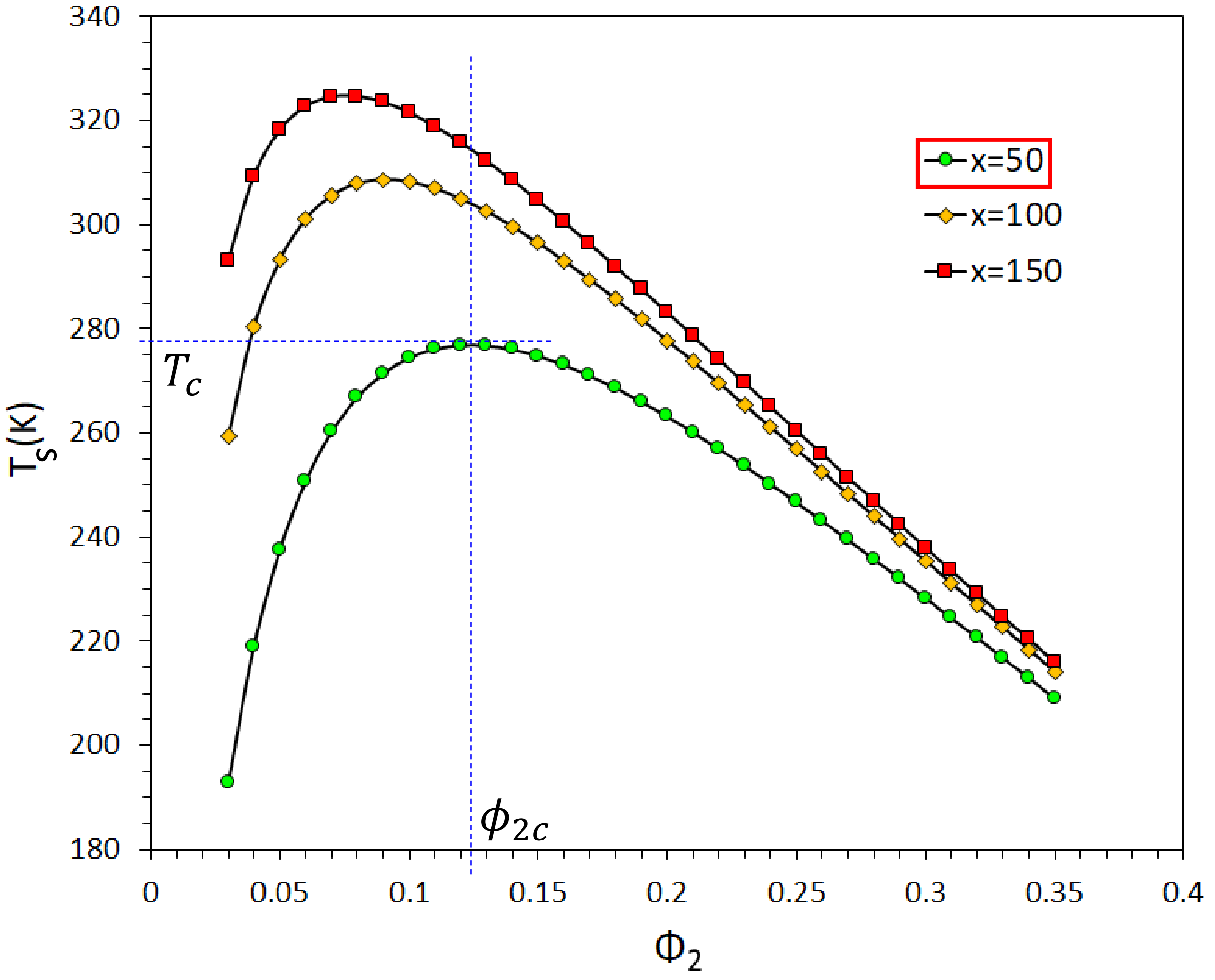
Thermodynamics of Polymer Blends



$$\phi_{2c} = \frac{1}{1+\sqrt{x}} = \frac{1}{1+\sqrt{50}} = 0.1239$$

$$T_c = \frac{b}{\frac{\left(1+\sqrt{x}\right)^2}{2x} - a}$$

$$= \frac{125}{\frac{\left(1+\sqrt{50}\right)^2}{2 \times 50} - 0.2} = 276.90 \text{ K}$$

SPINODAL CURVE: T_s vs ϕ_2

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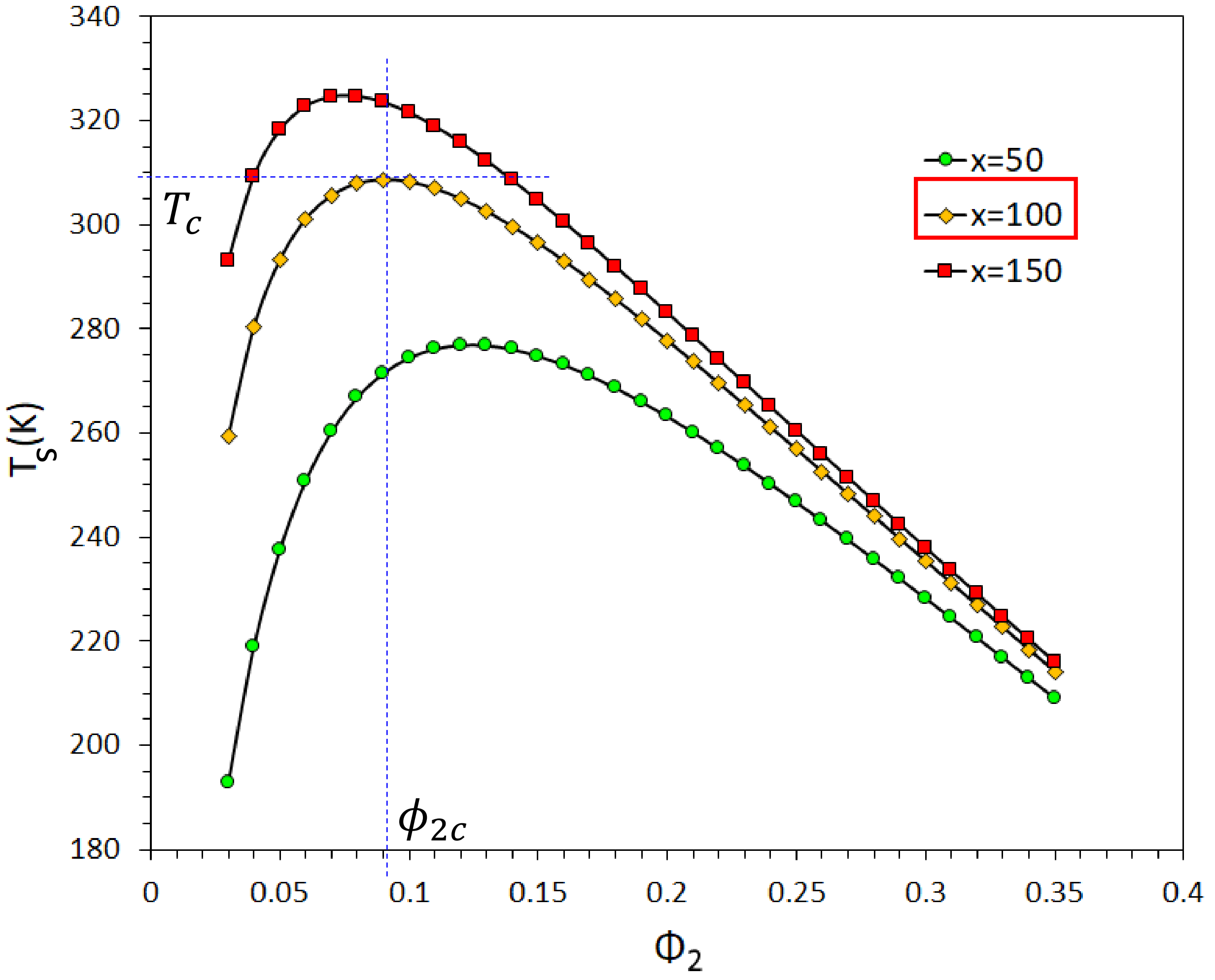
$$\chi = a + \frac{b}{T}$$

$$T_s = \frac{b}{\frac{1}{2}\left[\frac{1}{(1-\phi_2)} + \frac{1}{\phi_2 x}\right] - a}$$

$$a = 0.2, b = 125$$



$$\phi_{2c} = \frac{1}{1+\sqrt{x}} = \frac{1}{1+\sqrt{100}} = 0.0909$$

$$T_c = \frac{b}{\frac{\left(1+\sqrt{x}\right)^2}{2x} - a}$$

$$= \frac{125}{\frac{\left(1+\sqrt{100}\right)^2}{2\times 100} - 0.2} = 308.64\ \mathrm{K}$$

SPINODAL CURVE: T_s vs ϕ_2

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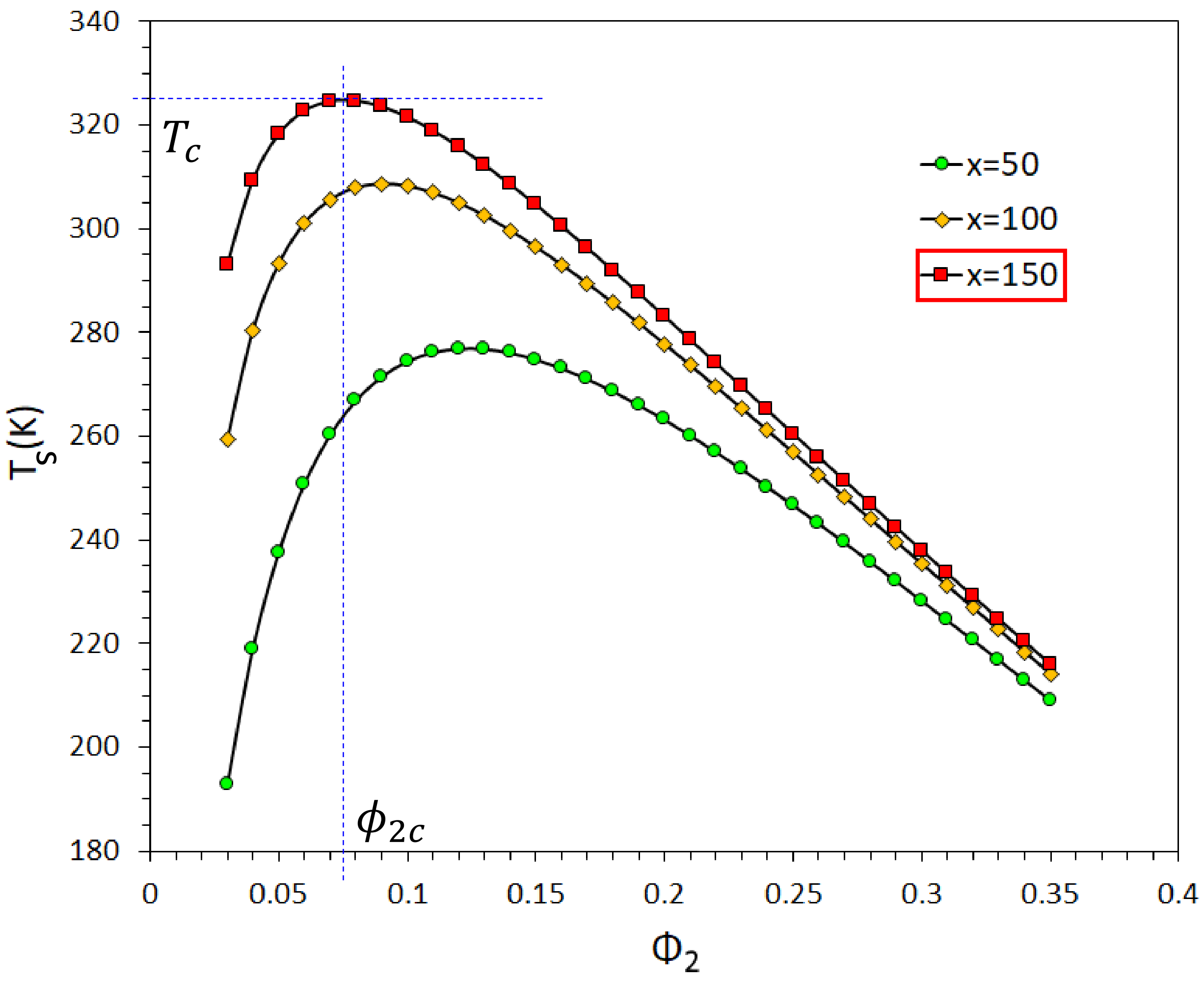
$$\chi = a + \frac{b}{T}$$

$$T_s = \frac{b}{\frac{1}{2}\left[\frac{1}{(1-\phi_2)} + \frac{1}{\phi_2 x}\right] - a}$$

$$a = 0.2, b = 125$$



$$\phi_{2c} = \frac{1}{1+\sqrt{x}} = \frac{1}{1+\sqrt{150}} = 0.0755$$

$$T_c = \frac{b}{\frac{\left(1+\sqrt{x}\right)^2}{2x} - a}$$

$$= \frac{125}{\frac{\left(1+\sqrt{150}\right)^2}{2\times 150} - 0.2} = 324.69\text{ K}$$

CRITICAL TEMPERATURE

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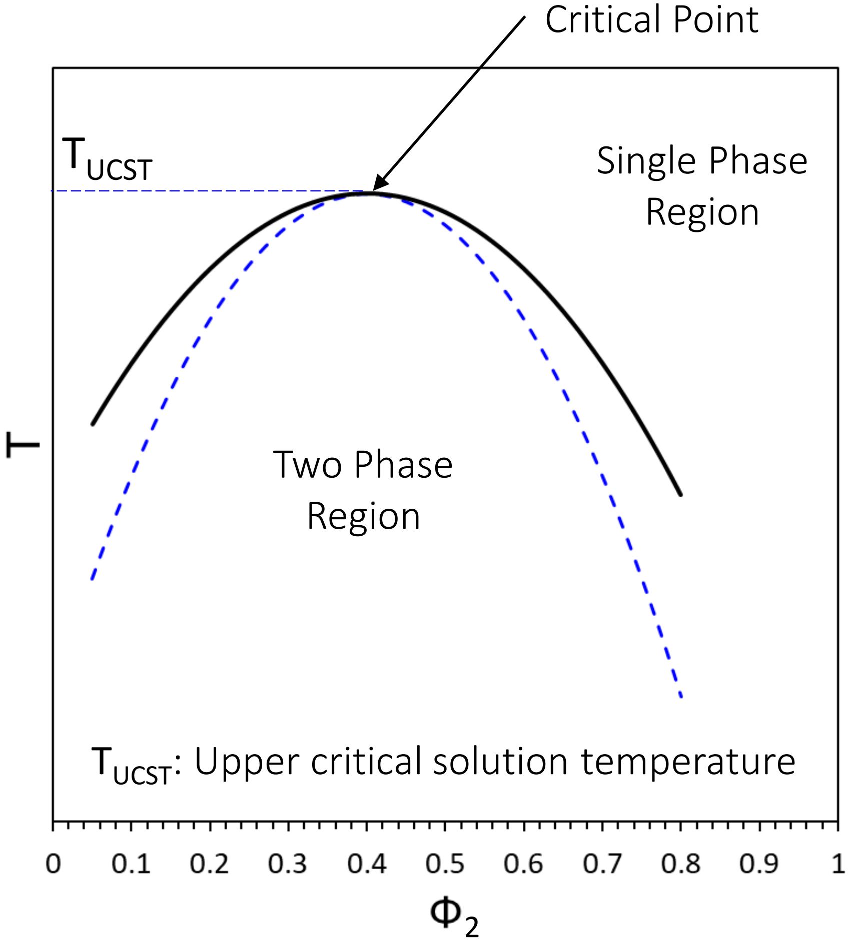
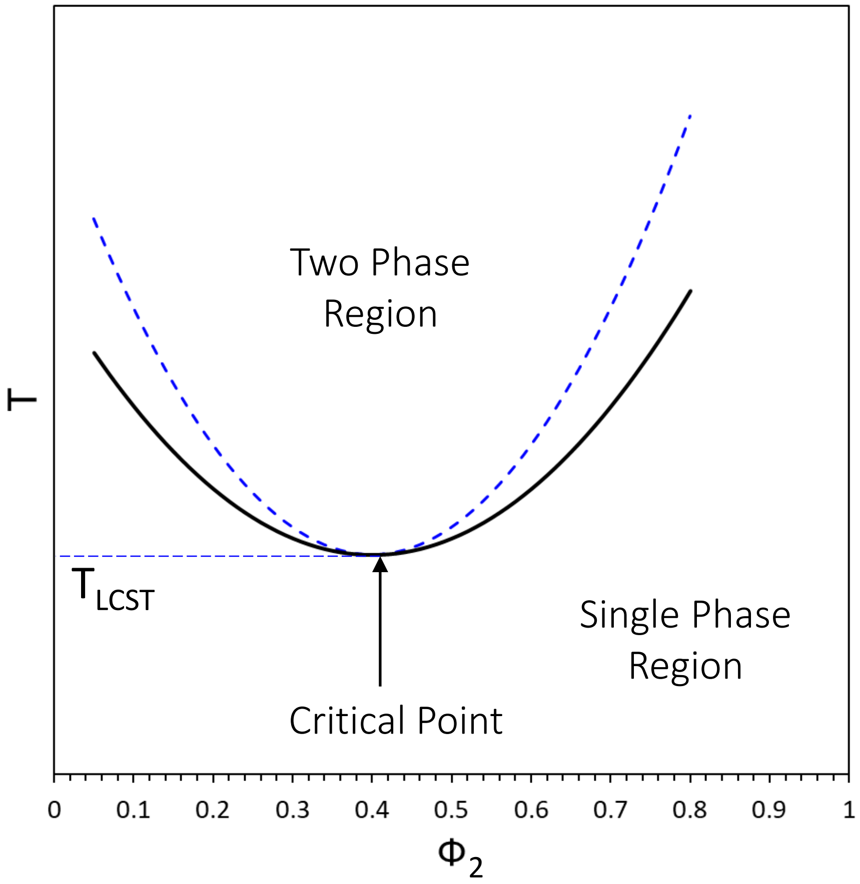
$$\chi = a + \frac{b}{T}$$

If $b > 0$,
χ decreases as T increases



If $b < 0$,
χ increases as T increases

T_{LCST}: Lower critical solution temperature



THERMODYNAMICS OF POLYMER BLENDS

EQUILIBRIUM: $\Delta G_{\mathrm{m}} = \Delta H_{\mathrm{m}} - T\Delta S_{\mathrm{m}} < 0$

For polymer blends, Flory-Huggins theory can be employed.

Polymer 1: x_1 segments per molecule

Polymer 2: x_2 segments per molecule

$$\phi_1 = \frac{x_1 N_1}{x_1 N_1 + x_2 N_2} \qquad \phi_2 = \frac{x_2 N_2}{x_1 N_1 + x_2 N_2}$$

$$\boxed{\begin{aligned}\Delta G_{\mathrm{m}} &= RT[n_1 \ln\phi_1 + n_2 \ln\phi_2 + x_1 n_1 \phi_2 \chi] \\ &= k_B T[N_1 \ln\phi_1 + N_2 \ln\phi_2 + x_1 N_1 \phi_2 \chi]\end{aligned}}$$

Flory-Huggins equation for Gibbs free energy change of mixing for polymer-polymer blend

χ: Flory-Huggins polymer-polymer interaction parameter

$$\Delta G_{\mathrm{m}} = k_B T[N_1 \ln\phi_1 + N_2 \ln\phi_2 + x_1 N_1 \phi_2 \chi]$$

$$\phi_1 = \frac{x_1 N_1}{x_1 N_1 + x_2 N_2} \qquad \phi_2 = \frac{x_2 N_2}{x_1 N_1 + x_2 N_2}$$

$$\overline{\Delta G}_{\mathrm{m}} = \frac{\Delta G_{\mathrm{m}}}{x_1 N_1 + x_2 N_2}$$

$$= k_B T\left[\frac{(1-\phi_2)}{x_1}\ln(1-\phi_2) + \frac{\phi_2}{x_2}\ln\phi_2 + (1-\phi_2)\phi_2\chi\right]$$