第三章　高分子溶液

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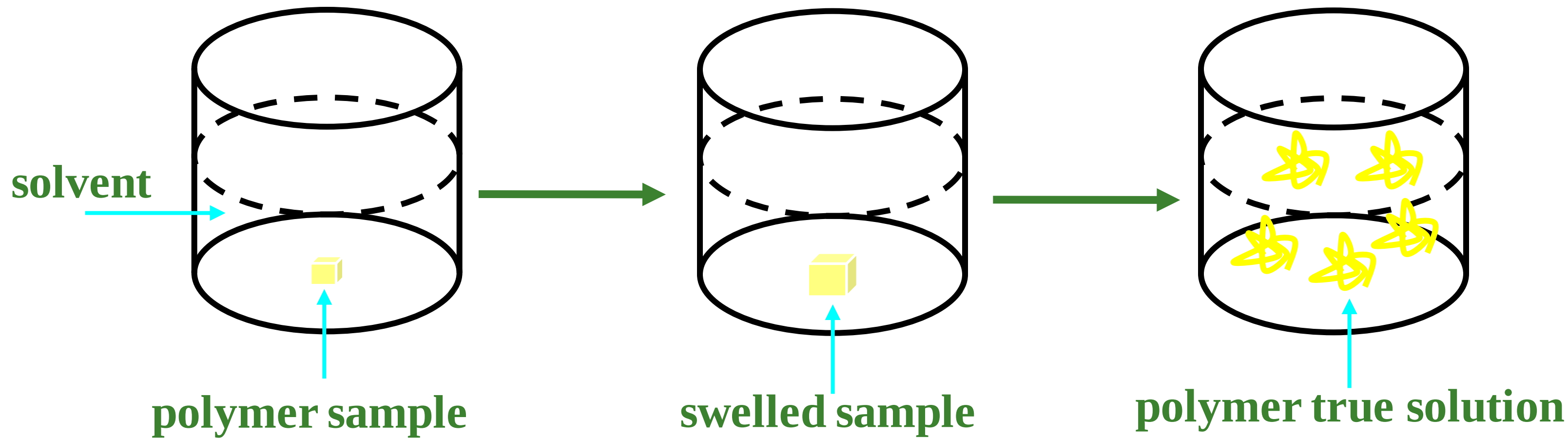
Chapt. 3 Polymer Solutions

➢ The solution process



➢ **This process is usually slower compared with small molecules, and strongly dependent on the chemical structures and condensed states of the samples.**

Crosslinked polymer: only can be swelled.
Crystalline PE: dissolve at the temperature approached to its melting temperature.
Crystalline Nylon 6,6: dissolved at room temperature by using the solvent with strong hydrogen bonds.

3.1 Criteria (判据) of Polymer Solubility

- **Gibbs free energy of mixing**

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

$$\Delta S_{mix} > 0$$

- **Solubility occurs only when the ΔG_{mix} is negative.**

1. Hildebrand enthalpy of mixing (混合焓)

1-1 + 2-2 ⟶ 1-2 + 1-2 **1: solvent; 2: polymer**

$$\Delta H_{mix} = \left(\frac{\Delta E_1}{v_1} + \frac{\Delta E_2}{v_2} - 2\sqrt{\frac{\Delta E_1 \Delta E_2}{v_1 v_2}} \right) P_{12}$$

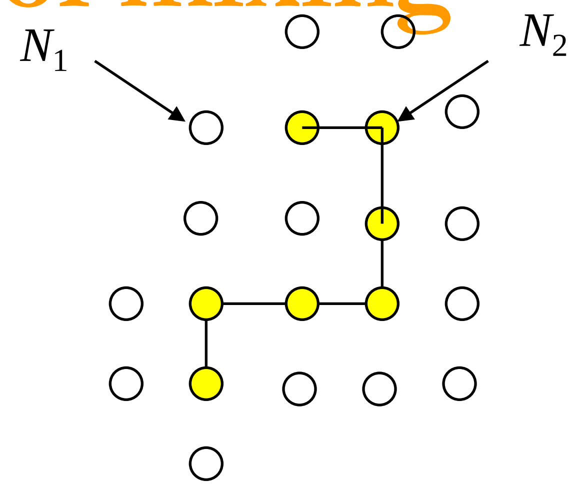
($\Delta E/v$) cohesive energy density (内聚能密度)

$$\Delta H_{mix} = V_m \phi_1 \left(\frac{n_2 \bar{V}_1}{V_m} \right) \left(\left(\frac{\Delta E_1}{v_1} \right)^{1/2} - \left(\frac{\Delta E_2}{v_2} \right)^{1/2} \right)^2 = V_m \phi_1 \phi_2 \left(\left(\frac{\Delta E_1}{v_1} \right)^{1/2} - \left(\frac{\Delta E_2}{v_2} \right)^{1/2} \right)$$

$$= V_m \phi_1 \phi_2 \left[\delta_1 - \delta_2 \right]^2$$

$\delta = (\Delta E/v)^{1/2}$: solubility parameter (溶度参数)

2. Huggin's Enthalpy of mixing



Different pairs in solution:

- solvent-solvent molecule: [1-1], ε_{11}
- solute-solute segment: [2-2], ε_{22}
- solvent-solute: [1-2], ε_{12}

Mixing process: $$\frac{1}{2}[1-1]+\frac{1}{2}[2-2]=[1-2]$$

$$\Delta\varepsilon_{12}=\varepsilon_{12}-\frac{1}{2}\left(\varepsilon_{11}+\varepsilon_{22}\right)$$

$$\phi_1=\frac{N_1}{N_1+xN_2} \quad \text{and} \quad \phi_2=\frac{xN_2}{N_1+xN_2}$$

$$\Delta H_{mixing}=P_{12}\Delta\varepsilon_{12} \qquad \boxed{P_{12}\text{ total pairs of [1-2]}}$$

$$P_{12}=\left[\underline{(Z-2)x+\cancel{2}}\right]\phi_1 N_2=(Z-2)N_1\phi_2$$

cells surrounding a polymer

number of polymers

volume fraction of solvent ~ Possibility of the cell occupied by solvent.

$$\Delta H_{mixing}=(Z-2)N_1\phi_2\Delta\varepsilon_{12}$$

$$\Delta H_{mixing}=kT\chi N_1\phi_2=RT\chi n_1\phi_2$$

$$=\frac{V_m}{V_s}kT\chi\phi_1\phi_2=V_m\phi_1\phi_2\left[\delta_1-\delta_2\right]^2/\tilde{N}$$

$$\boxed{\chi=\frac{(Z-2)\Delta\varepsilon_{12}}{kT}=\frac{V_s\left(\delta_1-\delta_2\right)^2}{RT}}$$

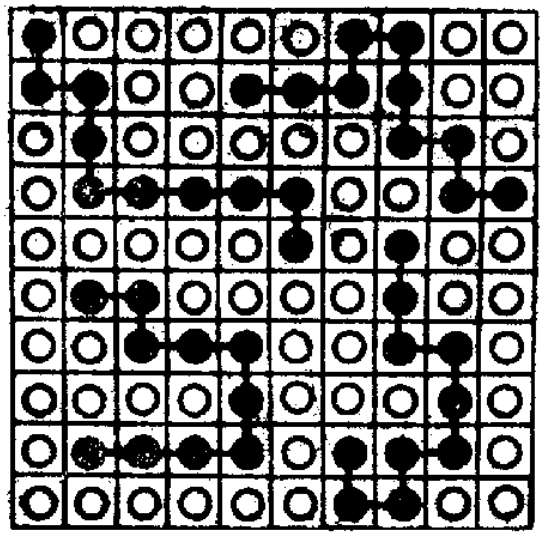
Flory-Huggins parameter: (interaction parameter)

3.2 Thermodynamics of Polymer Solutions

(1) Entropy of mixing for ideal solution

$$\Delta S_{mix}^{i} = -k\left(N_1 \ln X_1 + N_2 \ln X_2\right)$$

(2) Entropy of mixing for polymer solutions



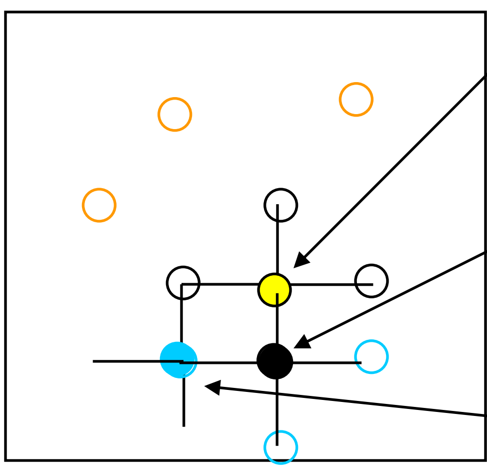
- **The lattice model assumes that the volume is unchanged during mixing.**
- **Each repeating unit of the polymer (segment) occupies one position in the lattice and so does each solvent molecule.**
- **The mixing entropy is strongly influenced by the chain connectivity of the polymer component.**

Flory-Huggins theory (Lattice Model (格子模型))

体系中有N_1个溶剂分子 + N_2个链段数为x的高分子

总格子数: $N=N_1+xN_2$

已有j个高分子放入, 剩下$N-xj$个空格, 求第$j+1$个高分子的放置方式W_{j+1}???



1. 放置第j+1个高分子的第1个链段的概率

$N-xj$

2. 放置第j+1个高分子的第2个链段的概率

$Z(N-xj-1)/N$

3. 放置第j+1个高分子的第3个链段的概率

$(Z-1)(N-xj-2)/N$ ....

x. 放置第x个链段的概率

$(Z-1)(N-xj-x+1)/N$

Entropy of mixing from FH theory

$$W_{j+1} = \underbrace{(N-xj)}_{\mathbf{1^{st}}} \times \underbrace{Z\left(\frac{N-xj-1}{N}\right)}_{\mathbf{2^{nd}}} \underbrace{\times (Z-1)\left(\frac{N-xj-2}{N}\right)}_{\mathbf{3^{rd}}} \underbrace{\times (Z-1)\left(\frac{N-xj-3}{N}\right)}_{\mathbf{4^{th}}} \cdots \underbrace{(Z-1)\left(\frac{N-xj-x+1}{N}\right)}_{\boldsymbol{x}^{\mathbf{th}}\ \mathbf{segment}}$$

$\mathbf{Z \approx Z-1}$

$$W_{j+1} = \left(\frac{Z-1}{N}\right)^{x-1} \frac{(N-xj)!}{(N-xj-x)!}$$

总方式

$$\Omega = \frac{1}{N_2!}\prod_{j=0}^{N_2-1} W_{j+1} = \frac{1}{N_2!}\left(\frac{Z-1}{N}\right)^{N_2(x-1)} \underbrace{\frac{N!}{\cancel{(N-x)!}}}_{\mathbf{1^{st}}} \underbrace{\frac{\cancel{(N-x)!}}{\cancel{(N-2x)!}}}_{\mathbf{2^{st}}} \cdots \underbrace{\frac{\cancel{(N-xN_2-x)!}}{(N-xN_2)!}}_{\boldsymbol{N_2}^{\mathbf{st}}\ \mathbf{chain}}$$

$$= \frac{1}{N_2!}\left(\frac{Z-1}{N}\right)^{N_2(x-1)} \frac{N!}{(N-xN_2)!}$$

Entropy of solution:

$$S_{solution} = k\ln\Omega = k\left[N_2(x-1)\ln\left(\frac{Z-1}{N}\right) + \ln N! - \ln N_2! - \ln(N-xN_2)!\right]$$

Entropy of mixing from FH theory

Using Stirling's approximation ($\ln x! \approx x\ln x - x$), we have:

$$S_{solution} = -k\left[N_1 \ln\frac{N_1}{N_1 + xN_2} + N_2 \ln\frac{N_2}{N_1 + xN_2} - N_2(x-1)\ln\frac{Z-1}{e}\right]$$

Entropy of the pure solvent and pure polymer: $S_{polymer} = kN_2\left[\ln x + (x-1)\ln\frac{Z-1}{e}\right]$ **($N_1 = 0$) and** $S_{solvent} = 0$

Therefore,

$$\boxed{\begin{aligned}\Delta S_{mixing} &= S_{solution} - (S_{solvent} + S_{polymer})\\ &= -k\left[N_1\ln\frac{N_1}{N_1+xN_2} + N_2\ln\frac{xN_2}{N_1+xN_2}\right] = -k\left[N_1\ln\phi_1 + N_2\ln\phi_2\right]\\ &= -R\left[n_1\ln\phi_1 + n_2\ln\phi_2\right]\\ &= -k\frac{V_m}{V_s}\left[\phi_1\ln\phi_1 + \frac{\phi_2}{x}\ln\phi_2\right]\end{aligned}}$$

where $\phi_1 = \frac{N_1}{N_1+xN_2} = \frac{n_1}{n_1+xn_2} = \frac{\tilde{N}n_1V_s}{V_m}$ **and** $\phi_2 = \frac{xN_2}{N_1+xN_2} = \frac{xn_2}{n_1+xn_2} = \frac{\tilde{N}xn_2V_s}{V_m}$

Free Energy of FH Theory

Huggins Enthalpy:

$$\Delta H_{mixing} = kT\chi N_1\phi_2 = RT\chi n_1\phi_2 = \frac{V_m}{V_s} RT\chi\phi_1\phi_2$$

Gibbs Free Energy:

$$\Delta G_{mixing} = kT\left(N_1 \ln\phi_1 + N_2 \ln\phi_2 + \chi x_1 N_1\phi_2\right)$$ 分子数

$$\Delta G_{mixing} = RT\left(n_1 \ln\phi_1 + n_2 \ln\phi_2 + \chi x_1 n_1\phi_2\right)$$ 摩尔数

$$\Delta G_{mixing} = kT\frac{V_m}{V_s}\left(\frac{\phi_1}{x_1}\ln\phi_1 + \frac{\phi_2}{x_2}\ln\phi_2 + \chi\phi_1\phi_2\right)$$ 一般通式

$$\phi_1 = \frac{x_1N_1}{x_1N_1 + x_2N_2} = \frac{x_1n_1}{x_1n_1 + x_2n_2} = \frac{\tilde{N}x_1n_1V_s}{V_m} \qquad \phi_2 = \frac{x_2N_2}{x_1N_1 + x_2N_2} = \frac{x_2n_2}{x_1n_1 + x_2n_2} = \frac{\tilde{N}x_2n_2V_s}{V_m}$$

For Polymer Solutions $x_1=1$

Chemical potentials (化学位):

$$\Delta\mu_1 = \left[\frac{\partial\left(\Delta G_{mixing}\right)}{\partial n_1}\right]_{T,P,n_2} = RT\left[\ln\phi_1 + \left(1-\frac{1}{x}\right)\phi_2 + \chi\phi_2^2\right]$$ **(for solvent)**

$$\Delta\mu_2 = \left[\frac{\partial\left(\Delta G_{mixing}\right)}{\partial n_2}\right]_{T,P,n_1} = RT\left[\ln\phi_2 - \left(x-1\right)\phi_1 + x\chi\phi_1^2\right]$$ **(for polymer)**

In the case of ϕ_2 << 1, $\ln\phi_1 = \ln\left(1-\phi_2\right) \approx -\phi_2 - \frac{1}{2}\phi_2^2 \cdots$

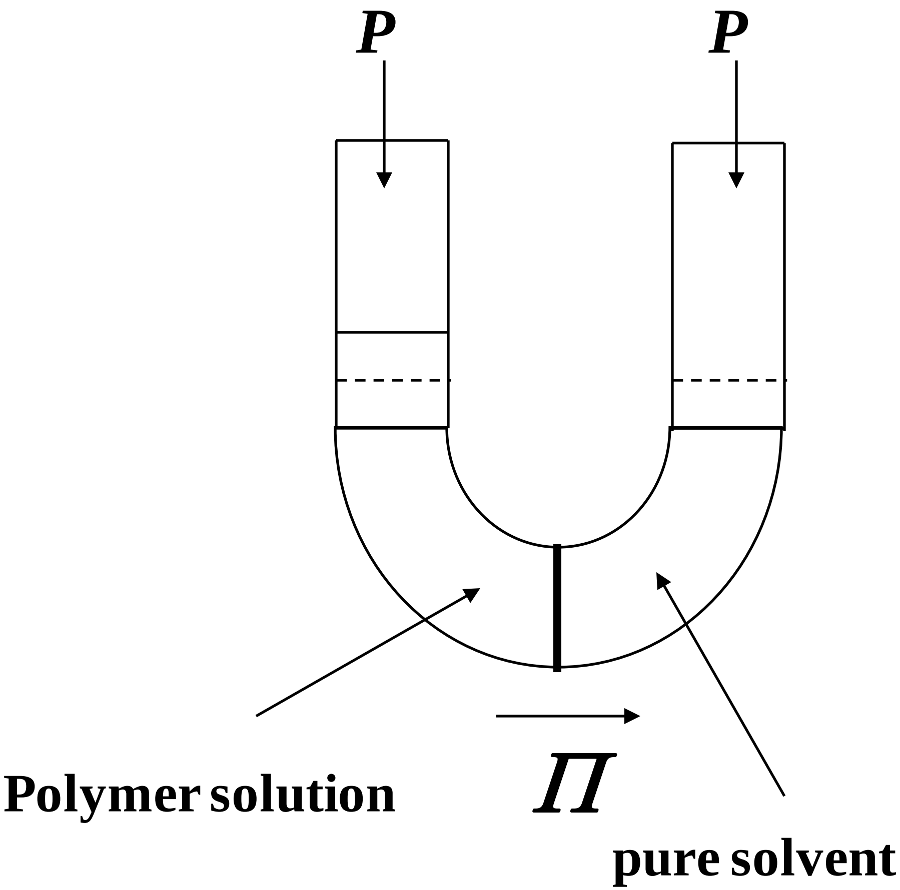
$$\Delta\mu_1 = RT\left[-\frac{1}{x}\phi_2 + \left(\chi - \frac{1}{2}\right)\phi_2^2 + w\phi_2^3\right]$$ $\chi=1/2$**,有热效应的"理想溶液"???**

→

$\chi < 1/2$, good solvent
$\chi = 1/2$, theta Θ solvent
$\chi > 1/2$, poor solvent

Osmotic pressure (渗透压):

$$\mu_s\left(\phi_2, P+\pi, T\right) = \mu_s\left(0, P, T\right)$$



$$\Pi = \frac{RT}{\bar{V}_1}\left(\phi_2 \frac{\partial F_m}{\partial \phi_2} - F_m\right) =$$

$$-\frac{\Delta\mu_1}{\bar{V}_1} = \frac{RT}{\bar{V}_1}\left[\underline{\frac{1}{x}}\phi_2 + \underline{\left(\frac{1}{2}-\chi\right)}\phi_2^2\right]$$

$$A_2 = \frac{\left(\frac{1}{2}-\chi\right)}{\bar{V}_1}$$ **second Virial coefficent**

当$\phi_2 << 1/x(0.5-\chi)$或$\chi=1/2$

$$\Pi = \frac{RT}{\bar{V}_1}\left[\frac{1}{x}\phi_2\right]$$

当$\phi_2 >> 1/x$, 即$\phi_2^2 >> \phi_2/x$

$\cancel{\Pi \sim \phi_2^2}$???

Appendix: **Osmotic pressure**

$$V = \left(N_p x + N_s\right) v_s \qquad \Delta G = kT \frac{V_m}{V_s} F$$

$$F\left(N_p, N_s, P, T\right) = F_m + PV = F_m + P\left(N_p x + N_s\right) v_s$$

$$\mu_s\left(\phi, P, T\right) = \mu_s^0 + kT\left(F_m - \phi \frac{\partial F_m}{\partial \phi}\right) + P v_s$$

$$\because \mu_s\left(\phi, P + \Pi, T\right) = \mu_s\left(0, P, T\right)$$

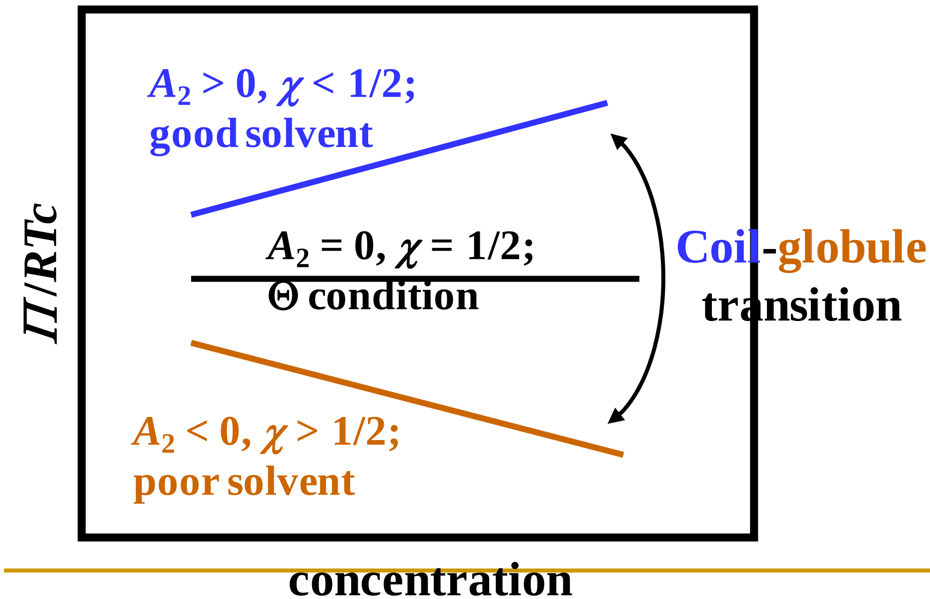
$$\mu_s^0 + kT\left(F_m - \phi \frac{\partial F_m}{\partial \phi}\right) + \left(P + \Pi\right) v_s = \mu_s^0 + P v_s$$

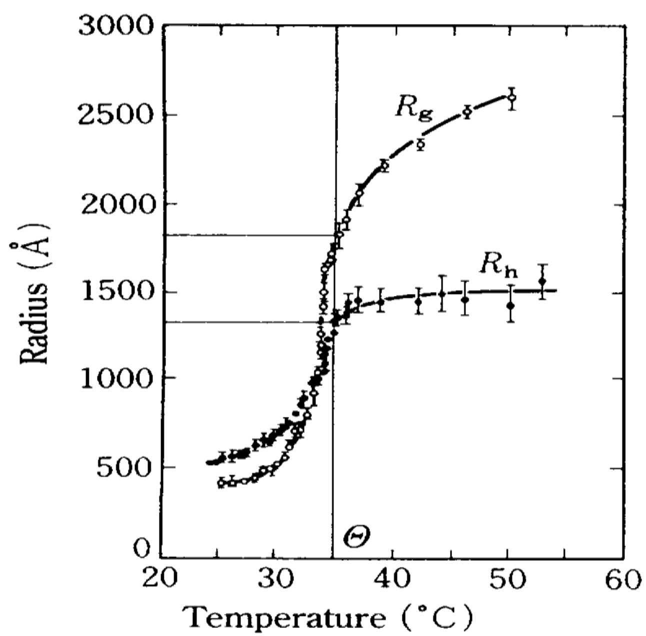
$$\therefore \Pi = \frac{kT}{v_s}\left(\phi \frac{\partial F_m}{\partial \phi} - F_m\right) = \frac{RT}{\bar{V}_1}\left(\phi \frac{\partial F_m}{\partial \phi} - F_m\right)$$

Polymer Shapes in Dilute Solutions

$$\Pi = \frac{RT}{\bar{V}_1}\left[\frac{1}{x}\phi_2 + \left(\frac{1}{2} - \chi\right)\phi_2^2\right]$$

- **Expanded, unperturbed, and collapsed chains**



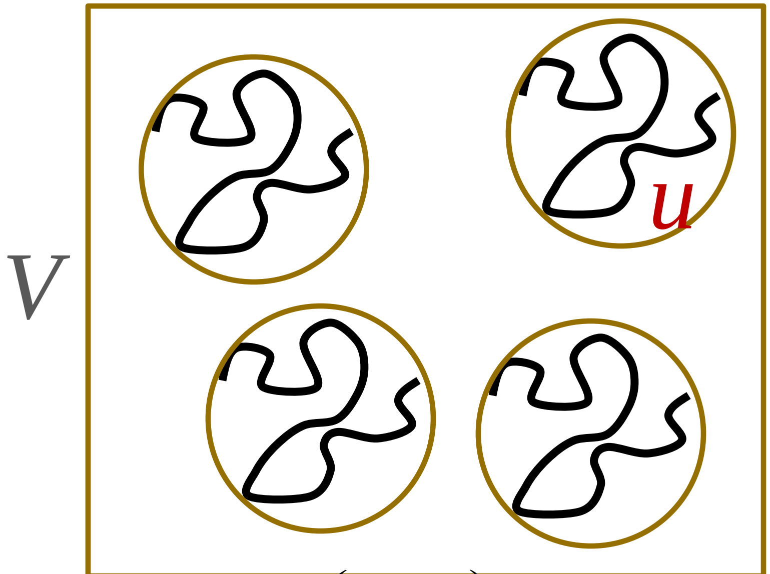


The coil-globule transition in a solution of polystyrene in cyclohexane. The radius of gyration R_g and the hydrodynamic radius R_h of the polymer show a dramatic change as temperature passes through the Θ temperature. (Sun, S.T.; etc. ***J. Chem. Phys.*** **1980**, *73*, 5971.)

$\chi \sim 1/kT$!!!

3.3 Chain Conformations in Dilute Solutions

(1) Flory-Krigbaum's Theory



有N_2个体积为u的“刚球”

两两刚球都不发生重叠的总概率

$$P \approx (V-u)^{(N_2-1)}(V-u)^{(N_2-2)}\dots(V-u)^0$$

$$P \approx V^{N_2}\left(1-\frac{u}{V}\right)^{N_2(N_2-1)/2} \qquad P \approx \prod_{i=0}^{N_2-1}(V-iu)$$

$$\ln\left(1-\frac{iu}{V}\right) \approx -\frac{iu}{V}$$

$$\Delta F \approx -T\Delta S = -kT\ln P$$

$$= -kT\left[N_2\ln V - \frac{N_2^2}{2}\frac{u}{V}\right]$$

$$\Pi = -\frac{\Delta\mu_1}{\tilde{V}_1} = -\frac{\partial \Delta F}{\partial V}$$

$$= RT\left[\frac{c}{M} + \boxed{\frac{\tilde{N}u}{2M^2}}c^2\right]$$

A_2

$$u \sim R_g^3 \sim T\,??$$

3.3 Chain Conformations in Dilute Solutions

(2) Flory 理论

ideal chain

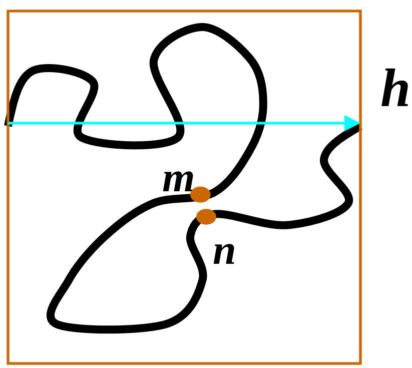
$$W_0(h,x)=\left(\frac{3}{2\pi x l^2}\right)^{3/2}\exp\left(-\frac{3h^2}{2xl^2}\right)4\pi h^2$$

real chain in solutions

$$Z(h,x)=W_0(h,x)P(h)\exp\left(-\frac{\bar{E}(h)}{kT}\right)$$

体积排除修正　　能量权重修正

(1) $P(h)$



链包含的体积 h^3　链段的体积 v_c

一个链段占有的体积分数 v_c/h^3

其他链段不与之发生重叠的概率 $(1-v_c/h^3)$

整条链两两链段都不发生重叠的总概率

$$P(h)\approx\prod_{i=0}^{x-1}\left(1-i\frac{v_c}{h^3}\right)$$

$$P(h)\approx\left(1-\frac{v_c}{h^3}\right)^{(x-1)}\left(1-\frac{v_c}{h^3}\right)^{(x-2)}\cdots\left(1-\frac{v_c}{h^3}\right)^{0}$$

溶液中真实单链的末端距概率分布函数*W*(*h*,*x*)

$$P(h) \approx \left(1-\frac{v_c}{h^3}\right)^{x(x-1)/2} = \exp\left(\frac{1}{2}x(x-1)\ln\left(1-\frac{v_c}{h^3}\right)\right) \approx \exp\left(-\frac{x^2}{2}\frac{v_c}{h^3}\right)$$

$$P(h) \approx \exp\left[\ln\prod_{i=0}^{x-1}\left(1-i\frac{v_c}{h^3}\right)\right] = \exp\left[\sum_{i=0}^{x-1}\ln\left(1-i\frac{v_c}{h^3}\right)\right] \approx \exp\left[-\frac{v_c}{h^3}\sum_{i=0}^{x-1}i\right]$$

(2) *E*(*h*)

$$\begin{aligned}\bar{E}(h) &= (z-2)x\phi_1\Delta\varepsilon_{12} = (z-2)x(1-\phi_2)\Delta\varepsilon_{12} \\ &= (z-2)x\Delta\varepsilon_{12} - (z-2)x\phi_2\Delta\varepsilon_{12} \\ &= const. - (z-2)x\frac{xv_c}{h^3}\Delta\varepsilon_{12}\end{aligned}$$

$$\frac{\bar{E}(h)}{kT} = C' - \chi\frac{x^2 v_c}{h^3}$$

$$Z(h,x) \propto h^2\exp\left[-\frac{3h^2}{2xl^2} - \frac{x^2}{2}\frac{v_c}{h^3}(1-2\chi)\right]$$

当χ=1/2, 理想高斯链

1. Polymer chain in good solvents – method I

$$\frac{\partial Z(h,x)}{\partial h}=0$$

$$\frac{\partial Z(h,x)}{\partial h}=\exp\left[-\frac{3h^2}{2xl^2}-\frac{x^2}{2}\frac{v_c}{h^3}(1-2\chi)\right]\underline{\left\{2h+h^2\left[-\frac{3h}{xl^2}+\frac{3x^2}{2}\frac{v_c}{h^4}(1-2\chi)\right]\right\}}=0$$

$$1-\frac{3h^{*2}}{2xl^2}+\frac{3x^2}{4}\frac{v_c}{h^{*3}}(1-2\chi)=0 \rightarrow \left(\frac{h^*}{h_0^*}\right)^5-\left(\frac{h^*}{h_0^*}\right)^3=\frac{9\sqrt{6}}{16}\frac{v_c}{l^3}x^{1/2}(1-2\chi)$$

$W_0(h,x)$的极值$h_0^*=(2xl^2/3)^{1/2}$

$$\boxed{h^* \propto h_0^*\left(\frac{x^{1/2}v_c}{l^3}(1-2\chi)\right)^{1/5} \propto x^{\nu}(1-2\chi)^{1/5}}$$

$\chi=1/2,\ \nu=1/2$

$\chi<1/2,\ \nu=3/5$

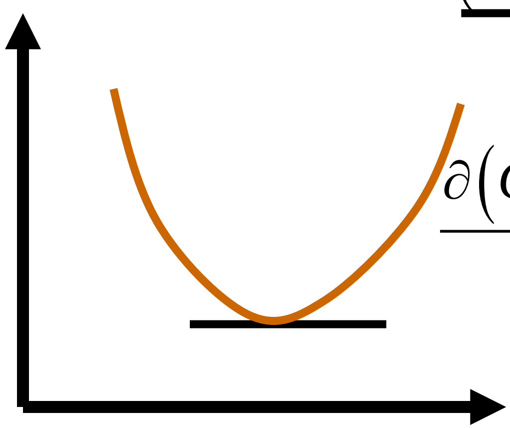
$\chi>1/2,\ \nu=??$

1. Polymer chain in good solvents - method II

$$G \sim -kT \ln Z \qquad Z(h,x) \propto \exp\left[-\frac{3h^2}{2xl^2} - \frac{x^2}{2}\frac{v_c}{h^3}(1-2\chi) + \ldots\right]$$

$$G \sim kT\left(\frac{3h^2}{2xl^2} + \frac{x^2 v_c}{2h^3}(1-2\chi) + \ldots\right) \qquad \phi_2 = \frac{xv_c}{h^3} \qquad \chi<1/2$$

$$G/h^3 \sim kT\left(\frac{3}{2xl^2h} + \frac{x^2 v_c}{2h^6}(1-2\chi) + \ldots\right) = kT\left(\frac{3}{2xl^2h} + \frac{\left(\frac{1}{2}-\chi\right)}{v_c}\phi_2^2 + \ldots\right)$$



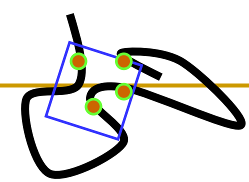
$$\frac{\partial\left(G/h^3\right)}{\partial h} = 0 \Rightarrow \boxed{h \sim x^{3/5}}$$

conformation entropy + two body interaction: second Virial coefficent

excluded volume repulsion

solvent-segment interaction

Two body interaction is very important



How to get ideal chain?

$$\chi = 1/2 \longrightarrow h^2 \sim N^1$$

$$\chi_\theta = \frac{(Z-2)\Delta\varepsilon_{12}}{kT_\theta} = \frac{V_s(\delta_1 - \delta_2)^2}{RT_\theta} = \frac{1}{2}$$

Θ Solution

$$T_\theta = \frac{2(Z-2)\Delta\varepsilon_{12}}{k} = \frac{2V_s}{R}(\delta_1 - \delta_2)^2$$

Θ Temperature

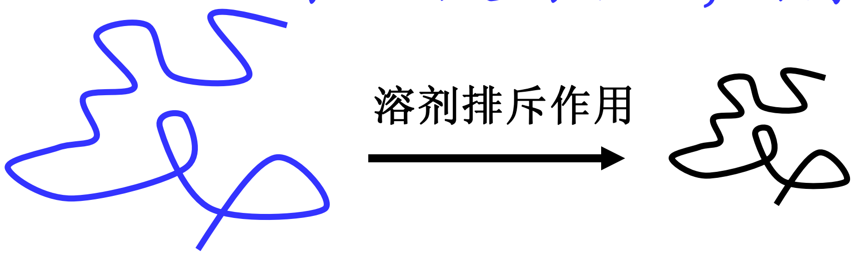
$$1-2\chi = 1 - \frac{\chi}{1/2} = \left(1 - \frac{T_\theta}{T}\right) = \tau$$

排除体积

$$u = v_c(1-2\chi) \approx l^3\tau$$

When does the freely jointed chain works—等效自由连接链

(1) 调节溶剂–链节的作用屏蔽掉体积排除效应和链节–链节相互作用 ⟶ 达到Θ温度的溶液, 测得无扰尺寸$\langle h^2 \rangle_0 \sim N$

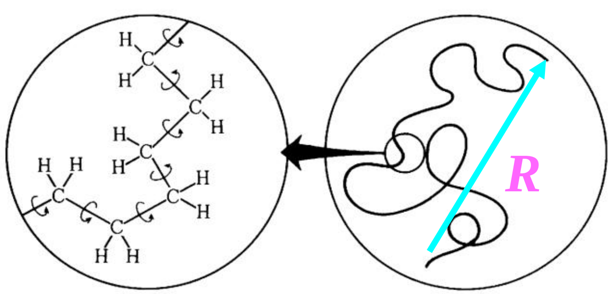


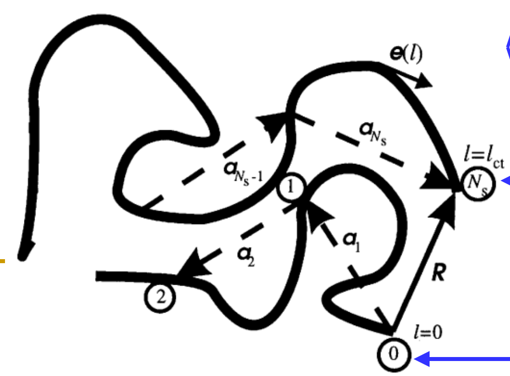
$$\langle h^2 \rangle \sim N^{6/5}\tau^{2/5} \qquad \langle h^2 \rangle_0 \sim N^1$$

(2) 降低高分子链的分辨率-消除局部刚性和旋转不自由

将链重新划分成有效链节数N_e和有效链节长度l_e

$$\langle h^2 \rangle_0 \sim N_e l_e^2$$





chain end

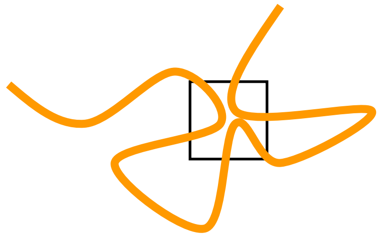
chain head

"Coarse-grained" (粗粒化) picture:

2. Polymer chain in poor solvents-Method I

$\chi > 1/2$

$h << h_0$



$$Z(h,x) \propto \exp\left[-\frac{3h^2}{2xl^2} - \frac{x^2}{2}\frac{v_c}{h^3}(1-2\chi) + \dots \right]$$

$$G \sim kT\left(\frac{3h^2}{2xl^2} + \frac{x^2 v_c}{2h^3}(1-2\chi) + ??? \right)$$

$$\phi_2 = x v_c / h^3$$

$$G/h^3 \sim \left(\frac{\left(\frac{1}{2}-\chi\right)}{v_c}\phi_2^2 + w\phi_2^3 \right) = \left[\frac{\left(\frac{1}{2}-\chi\right)}{v_c}\left(\frac{x v_c}{h^3}\right)^2 + w\left(\frac{x v_v}{h^3}\right)^3 \right]$$

second Virial coefficent
two body interaction:
excluded volume repulsion
solvent-segment interaction

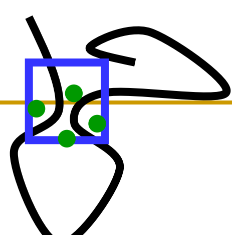
+

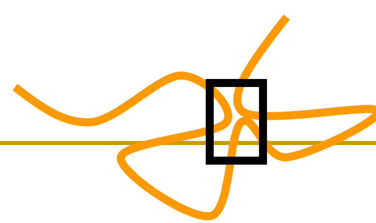
third Virial coefficent
three body repulsion

$G=0$

$$\boxed{h^3 \sim x(-\tau)^{-1}}$$

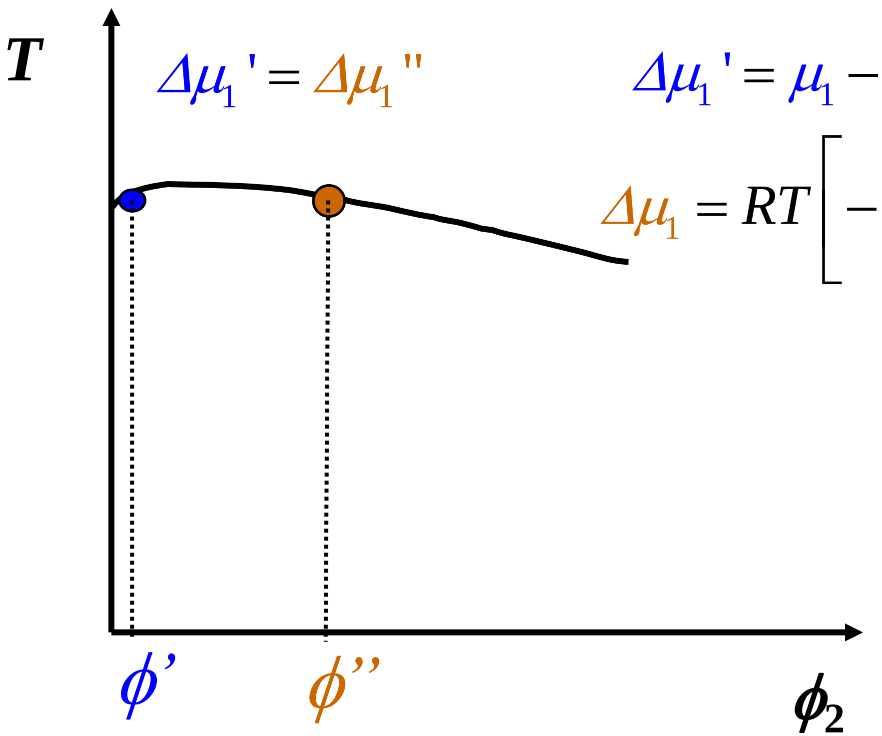
Three body interactions becomes important





2. Polymer chain in poor solvents-Method II

$$\Delta\mu_1 = RT\left[-\frac{1}{x}\phi_2 + \left(\chi - \frac{1}{2}\right)\phi_2^2 + w\phi_2^3\right]$$



$$\Delta\mu_1' = \Delta\mu_1''$$

$$\Delta\mu_1' = \mu_1 - \mu_1^0 \approx 0\Big|_{\phi_2'\to 0}$$

$$\Delta\mu_1 = RT\left[-\frac{1}{x}\phi_2'' + \left(\chi - \frac{1}{2}\right)\phi''^2_2 + w\phi''^3_2\right] = 0, \quad x \to \infty$$

$$\phi_2'' \sim 3\left(\chi - \frac{1}{2}\right)$$

In Polymer rich Phase:

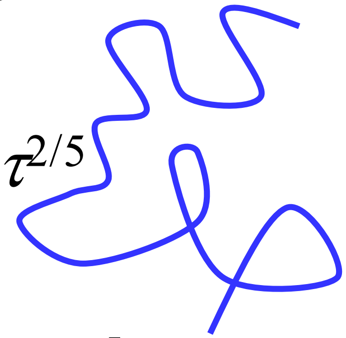
Concentration in Coil: $\phi_{in} = \dfrac{xv_c}{h^3} \approx \phi_2''$

$$h \sim v_c^{1/3} x^{1/3} (\chi - 1/2)^{-1/3} \sim v_c^{1/3} x^{1/3} (-\tau)^{-1/3}$$

Polymer Shapes in Dilute Solutions

(1) Polymer in a good solvent

$<h^2> \sim <S^2> \sim N^{6/5}\tau^{2/5}$

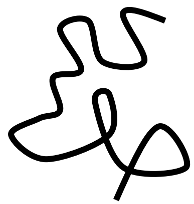


$$\chi = \frac{(Z-2)\Delta\varepsilon_{12}}{kT}$$

χ**~1/*kT***

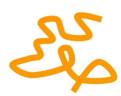
(2) Polymer in a Θ solvent

$<h^2> \sim <S^2> \sim N^1$



$T\downarrow$ $\chi\uparrow$

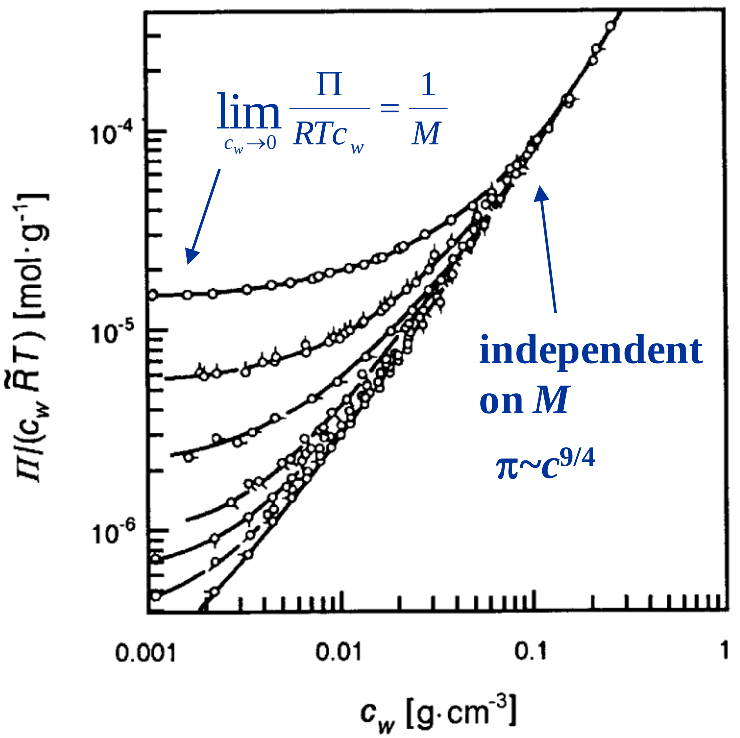
(3) Polymer in a poor solvent



$<h^2> \sim <S^2> \sim N^{2/3}|\tau|^{-2/3}$

Coil-globule transition

3.4 Semi-dilute Solutions of Polymers



$$\Pi = \frac{RT}{\bar{V}_1}\left[\frac{1}{x}\phi_2 + \left(\frac{1}{2} - \chi\right)\phi_2^2\right]$$

Osmotic pressure measured for samples of poly(α-methylstyrene) dissolved in toluene (25 °C). Molecular weight vary between *M* = 7 × 10⁴ (uppermost curve) and *M* = 7.47 × 10⁶ (lowest curve). (Noda,I.; et al. *Macromolecules* **1981**, *14*, 668.)

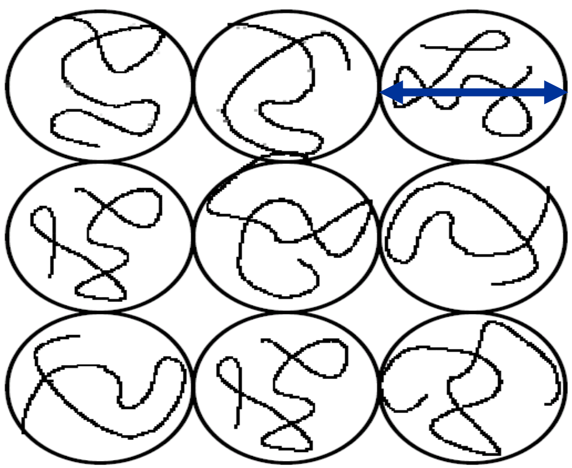
$\phi_2 << 1$ $\qquad$ $\phi_2^2 >> \phi_2 / x$

$\Pi/c \sim c^0$ $\qquad$ $\cancel{\Pi/c \sim c^1}$

$\Pi/c \sim c^{5/4}$

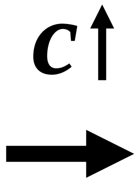
overlap concentration *c**

Semi-dilute regime: *c* = *c**

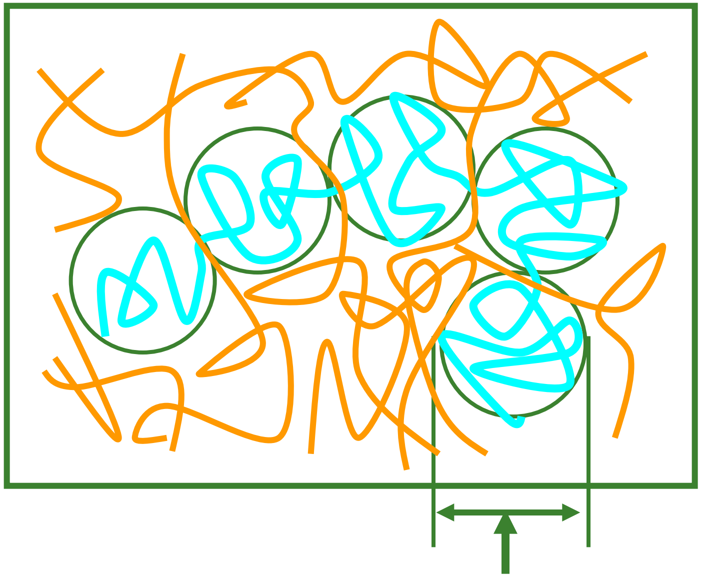


$$c^* = \frac{M}{\langle S^2 \rangle^{3/2}} \sim \frac{N}{N^{3\nu}} \sim N^{1-3\nu} \sim N^{-4/5}\tau^{-3/5}$$

For good solvent, *ν* = 3/5

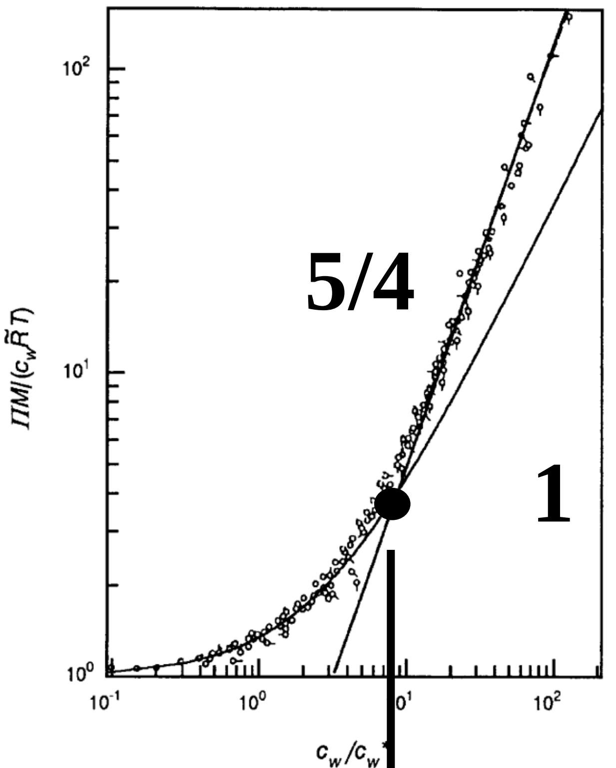


Semi-dilute regime: *c* > *c**



Apparent correlation length (表观相关长度) $\xi_{app} >> l_e$

Scaling Law of semi-dilute solution



$$\Pi = \frac{c}{N} k_B T f\left(\frac{c}{c^*}\right)$$

- **Osmotic pressure:**

$$\Pi = \frac{c}{N} k_B T \left(\frac{c}{c^*}\right)^m \quad \begin{cases} = \dfrac{c}{N} k_B T & (c = c^*) \\ = \dfrac{c}{N} k_B T c^m N^{m(3\nu-1)} & (c \geq c^*) \end{cases}$$

$$c^* \sim N^{1-3\nu}$$

In semi-dilute regime, Π is independent on *N*:

$$m(3\nu - 1) - 1 = 0$$

For good solvent,
ν = 3/5, therefore *m* = 5/4.

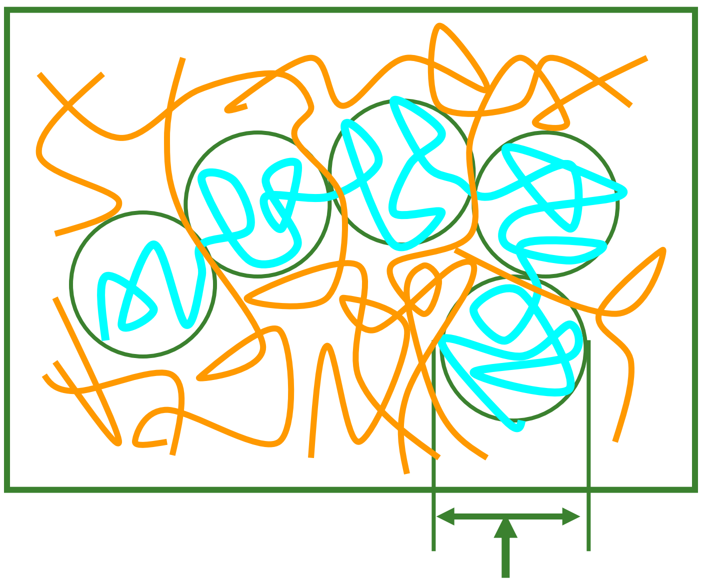
$$\boxed{\Pi \propto c^{1+m} \propto c^{9/4}}$$

Apparent correlation length ξ_{app}:

$$\xi_{app} \propto N^{\nu}\tau^{1/5}\left(\frac{c}{c^*}\right)^m \propto S = N^{\nu} \qquad (c = c^*)$$

$$\propto N^{\nu}c^m N^{m(3\upsilon-1)}\tau^{(1+3m)/5} \qquad (c \geq c^*)$$

$$c^* \propto N^{1-3\nu}$$



ξ_{app}

$$\xi_{app} = Sf\left(\frac{c}{c^*}\right)$$

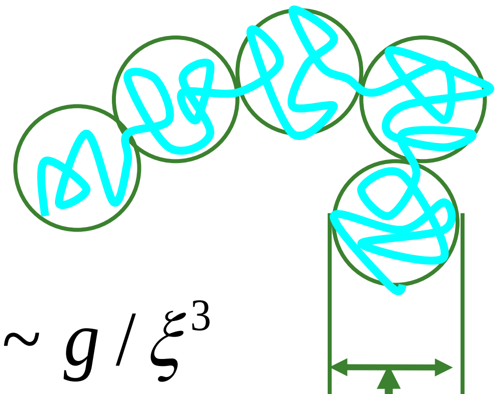
ξ_{app} is independent on N:

$$\nu + m(3\nu - 1) = 0$$

For good solvent, ν = 3/5, therefore m = -3/4.

$$\boxed{\xi_{app} \propto c^{-3/4}\tau^{-1/4}}$$

Polymer Shapes in Semi-dilute Solutions



$$c \sim g / \xi^3$$

$\xi_{app} \sim c^{-3/4}\tau^{-1/4}$

blob model:
由N'个串滴单元组成的理想链

$$\langle S^2 \rangle = N' l'^2$$

串滴内- 由N''个单元组成的扩张(良溶剂下)的短链

$$\langle \xi_{app}^2 \rangle \sim N''^{6/5} l^2 \tau^{2/5}$$

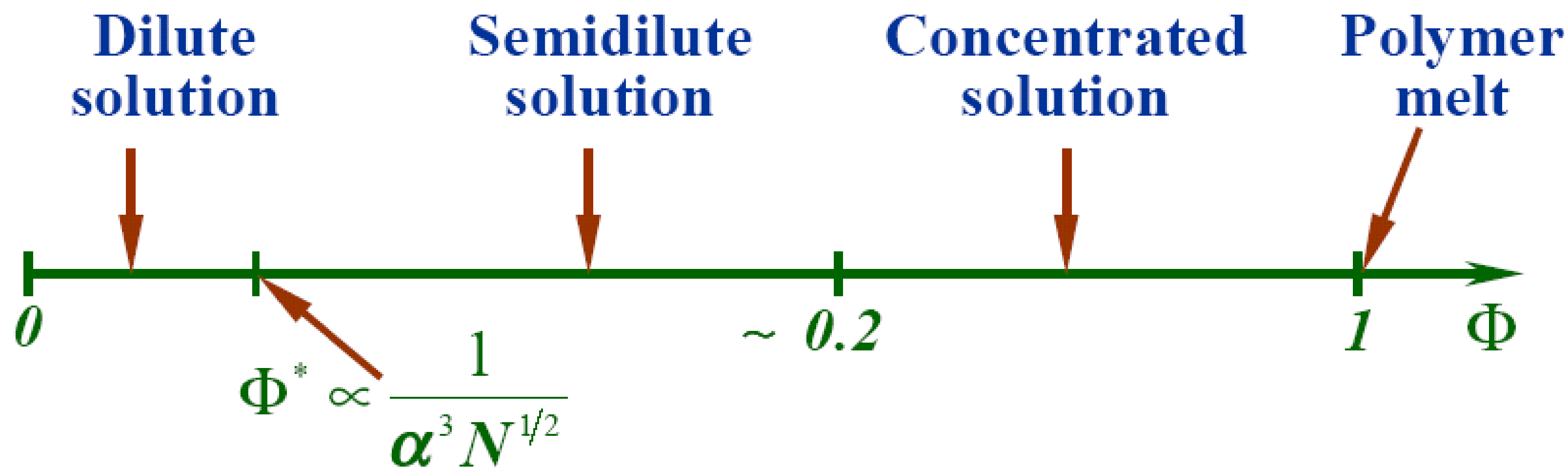
串滴内有$N''=g$个链段单元, 串滴数$N'=N/g$, 每个串滴大小$l'=\xi_{app}$

$$\xi_{app} \sim g^{3/5}\tau^{1/5}$$

$$g \sim \xi_{app}^{5/3}\tau^{-1/3} \sim c^{-5/4}\tau^{-3/4}$$

$$\langle S^2 \rangle_{\text{semi-dilute}} \sim \frac{N}{g}\xi_{app}^2 \sim \frac{N}{c^{-5/4}} c^{-6/4}$$

$$\langle S^2 \rangle_{\text{semi-dilute}} \sim N c^{-1/4}\tau^{1/4}$$



$\xi_{\text{app}} >> S$ $\qquad$ $\xi_{\text{app}} \le S$ $\qquad$ $\xi_{\text{app}} \sim l_e << S$

$\langle S^2 \rangle_{\text{dilute}} \sim N^{2\nu}$ $\qquad$ $\langle S^2 \rangle_{\text{semi-dilute}} \sim Nc^{-1/4}$ $\qquad$ $\langle S^2 \rangle_{\text{concentrated}} \sim N$

The presence of monomers from the other chains begins to "screen" (屏蔽) the intramolecular excluded volume interactions.

实质

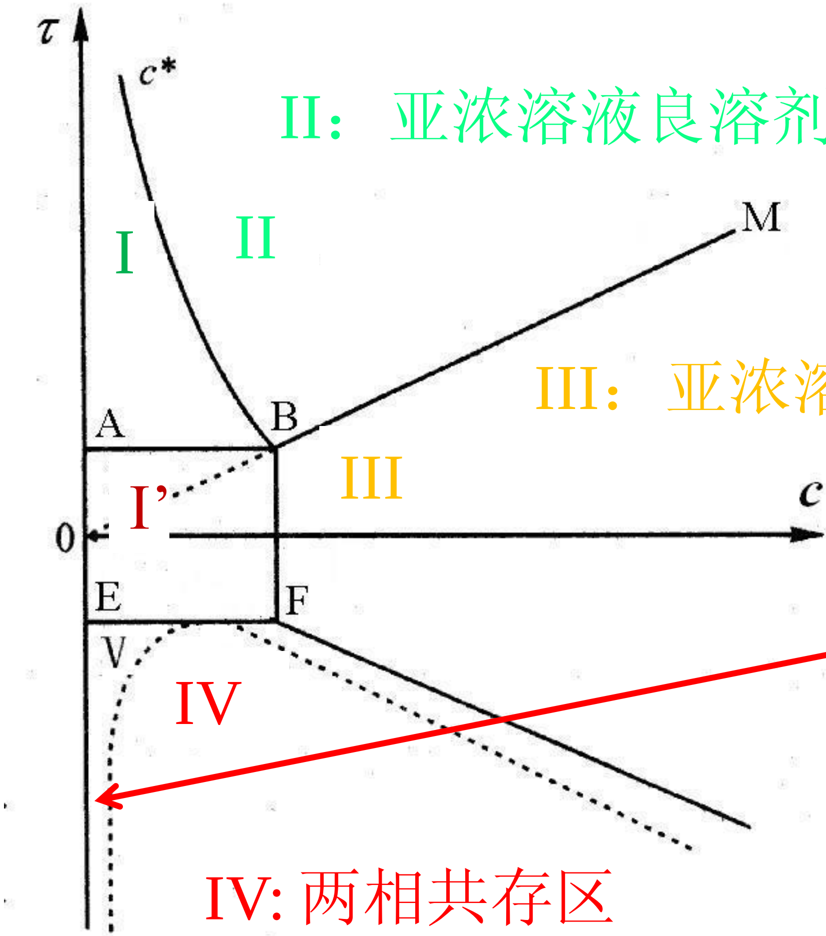
亚浓溶液: 串滴(blobs)在溶液中的分布达到均匀, 链段分布未达均匀

浓溶液: 链段在溶液中的分布完全均匀

Regions of the Polymer-Solvent Phase Diagram

I：稀溶液良溶剂区 $R_g \sim N^{3/5}\tau^{1/5}$

II：亚浓溶液良溶剂区 $R_g \sim N^{1/2}c^{-1/8}\tau^{1/8}$



III：亚浓溶液θ溶剂区 $R_g \sim N^{1/2}$

I'：稀溶液θ溶剂区 $R_g \sim N^{1/2}$

V：塌陷区 $R_g \sim N^{1/3}|\tau|^{-1/3}$

IV: 两相共存区

$R_g \sim (N/|\tau|)^{-1/3}$ 稀相

$R_g \sim N^{1/2}$ 浓相

c*方程: $c^* = N^{-4/5}\tau^{-3/5}$

BM 方程：$c = \tau$

AB 方程：$\tau = N^{-1/2}$

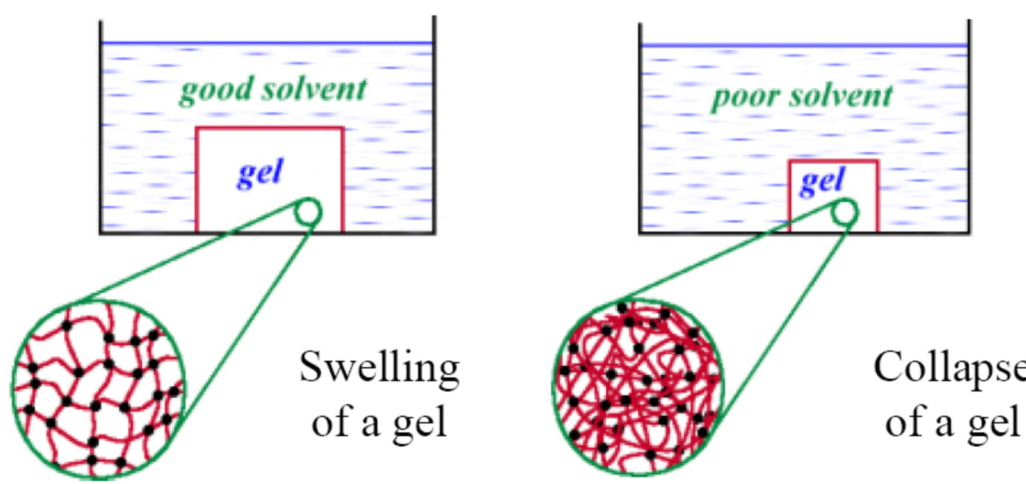
EF 方程：$\tau = -N^{-1/2}$

3.5 Concentrated Solutions of Polymers

1. 高分子-增塑剂

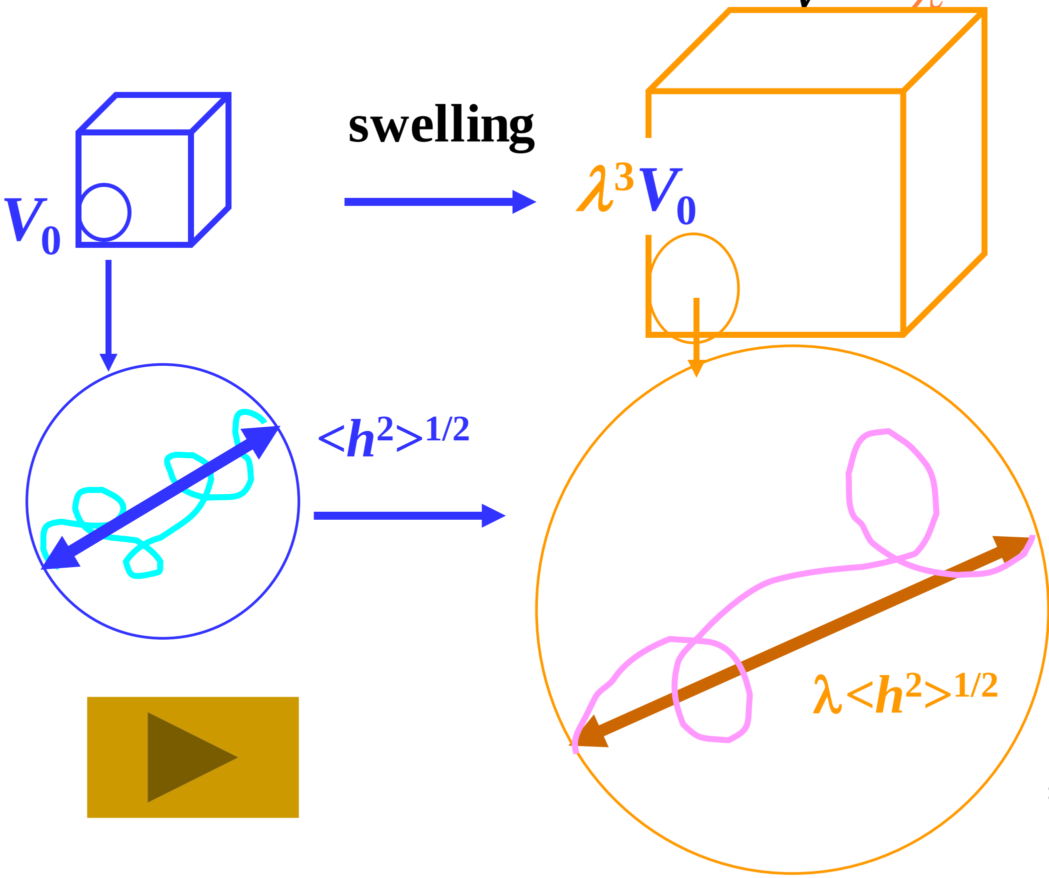
2. 纺丝液

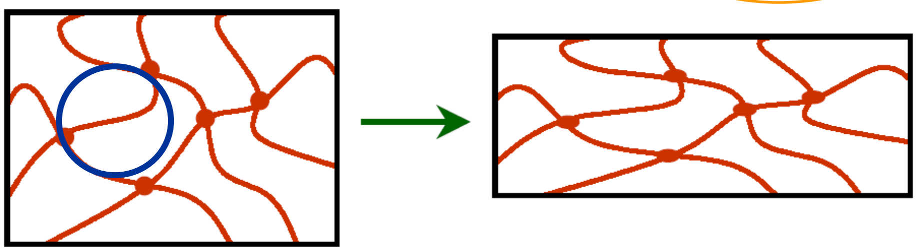
3. 凝胶和冻胶



Flory-Huggins free energy of a gel

$$\phi_2 = \frac{V_0}{V} = \frac{1}{\lambda^3}$$





$$\Delta F = \Delta F_{mixing} + \Delta F_{elastic}$$

$$\Delta F_{mixing} = RT\left[n_1 \ln \phi_1 + n_2 \ln \phi_2 + \chi n_1 \phi_2\right]$$

$$S = k \ln \Omega \sim k \ln \Phi\left(\boldsymbol{R}, N\right)$$

$$\Delta F_{elastic} = -T \Delta S_{elastic}$$

$$= NkT\left(\frac{3}{2h_0^2}\right)\left(\lambda^2 \bar{x}^2 + \lambda^2 \bar{y}^2 + \lambda^2 \bar{z}^2\right)$$

$$-NkT\left(\frac{3}{2h_0^2}\right)\left(\bar{x}^2 + \bar{y}^2 + \bar{z}^2\right)$$

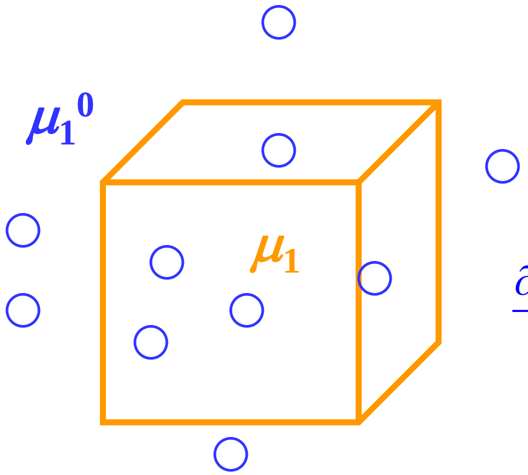
$$\bar{x}^2 = \bar{y}^2 = \bar{z}^2 = \frac{1}{3} h_0^2$$

$$= \frac{1}{2} NkT\left(3\lambda^2 - 3\right)$$

$$N = \frac{N/N_a M/V_0}{M} V_0 N_a = \frac{\rho_2}{\bar{M}_c} V_0 N_a$$

$$\Delta F_{elastic} = \frac{3}{2} \frac{\rho_2 V_0}{\bar{M}_c} RT\left(\phi_2^{-2/3} - 1\right)$$

Basic Equation of Gel Swelling



$$\mu_1=\mu_1^0 \qquad \Delta\mu_1=\mu_1-\mu_1^0=0$$

$$\Delta\mu_1=\frac{\partial\Delta F}{\partial n_1}=\frac{\partial\Delta F_m}{\partial n_1}+\frac{\partial\Delta F_{el}}{\partial\phi_2}\frac{\partial\phi_2}{\partial n_1}=0$$

$$\frac{\partial\Delta F_m}{\partial n_1}=RT\left[\ln\left(1-\phi_2\right)+\left(1-\frac{1}{x}\right)\phi_2+\chi\phi_2^2\right] \qquad \frac{\partial\Delta F_{elastic}}{\partial\phi_2}=-\frac{\rho_2 V_0}{\bar{M}_c}RT\phi_2^{-5/3}$$

$$=RT\left(\chi-\frac{1}{2}\right)\phi_2^2 \qquad \frac{\partial\Delta F_{elastic}}{\partial\phi_2}\frac{\partial\phi_2}{\partial n_1}=\frac{\rho_2 V_1}{\bar{M}_c}RT\phi_2^{1/3}$$

$$\ln\left(1-\phi_2\right)\doteq-\phi_2-\frac{1}{2}\phi_2^2 \qquad x\rightarrow\infty$$

$$\Delta\mu_1\doteq\left(\chi-\frac{1}{2}\right)\phi_2^2+\frac{\rho_2 V_1}{\bar{M}_c}\phi_2^{1/3}=0$$

$$\frac{\partial\phi_2}{\partial n_1}=\frac{\partial\left(\dfrac{V_0}{V_0+n_1V_1}\right)}{\partial n_1}=-\frac{V_0}{\left(V_0+n_1V_1\right)^2}V_1=-\phi_2^2\frac{V_1}{V_0}$$

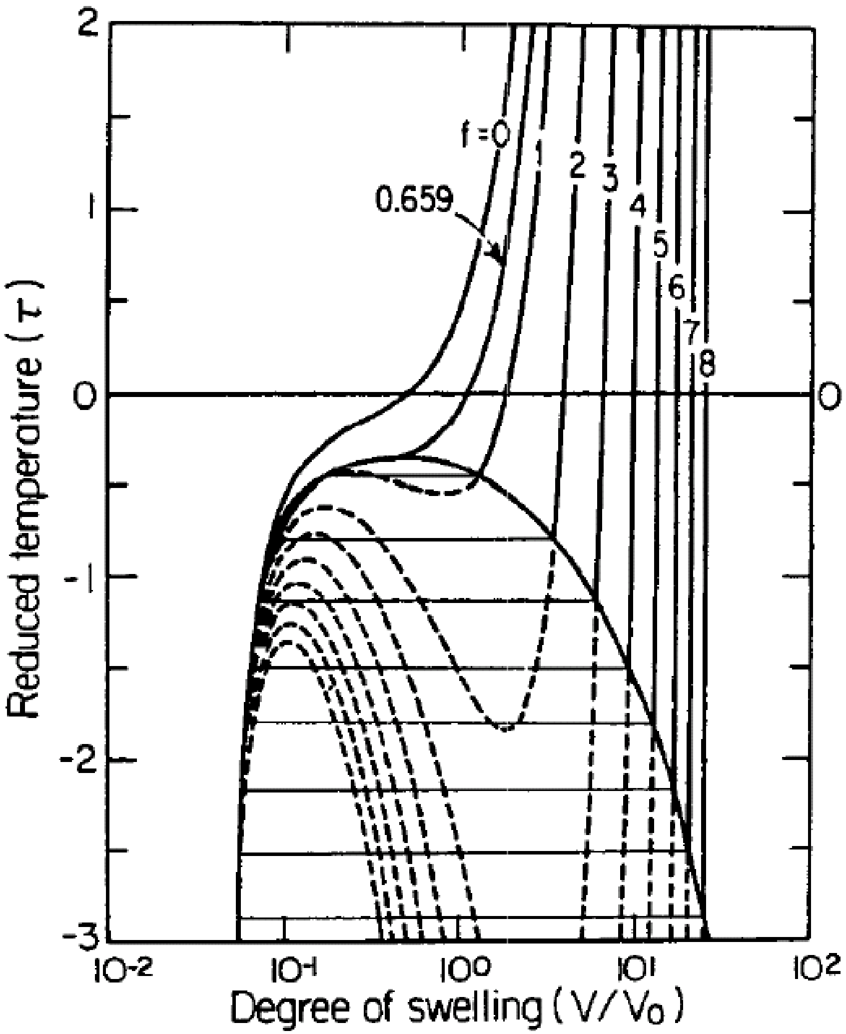
$$\boxed{\left(\frac{1}{2}-\chi\right)\frac{\bar{M}_c}{\rho_2 V_1}=Q^{5/3}} \Rightarrow$$

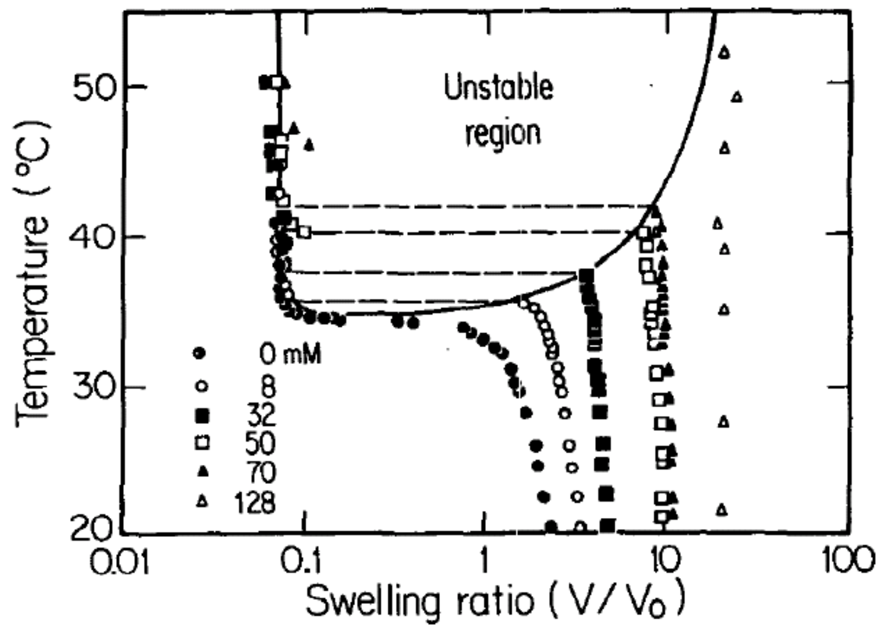
(1) 求χ

(2) 求M

$$Q=V/V_0=1/\phi_2$$

Volume Phase Transition of Gels

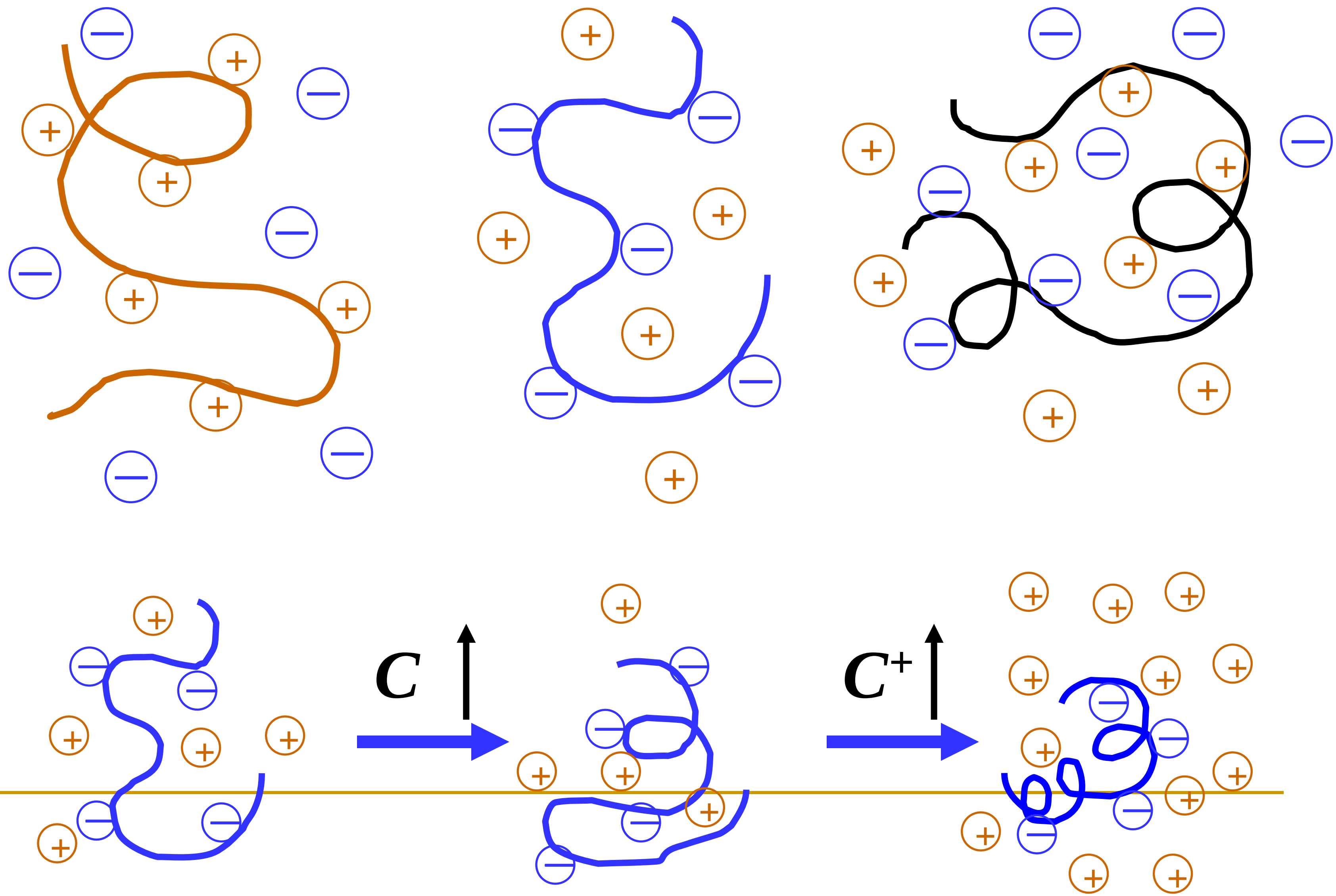




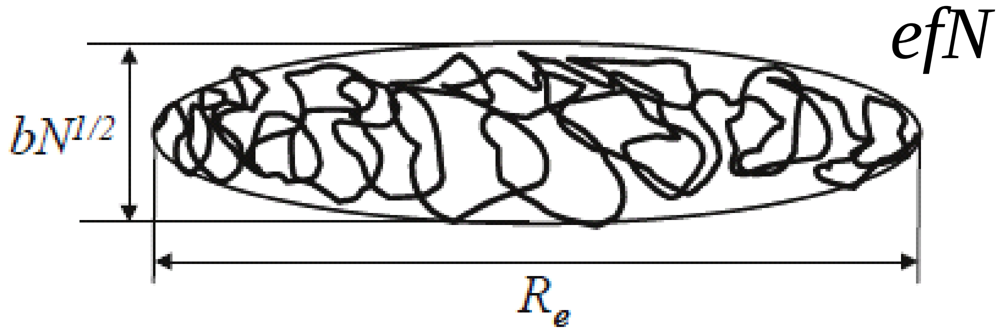
Experiment

Theory, τ=1-2χ~ 1-T_θ/T

3.6 Solutions of Polyelectrolytes



Theoretical Model of Polyelectrolytes



$$\frac{F(R_e)}{k_B T} = \frac{F_{\text{conf}}(R_e)}{k_B T} + \frac{F_{electr}(R_e)}{k_B T}$$

$$\frac{F_{\text{conf}}(R_e)}{k_B T} \approx \frac{R_e^2}{Nb^2} \qquad \frac{F_{electr}(R_e)}{kT} \approx \frac{l_{\text{B}}(fN)^2}{R_e} \ln\left(\frac{R_e}{N^{1/2}b}\right)$$

l_{B}为**Bjerrum**长度 $l_{\text{B}} = e^2/(\varepsilon kT) \quad u = l_B / b$

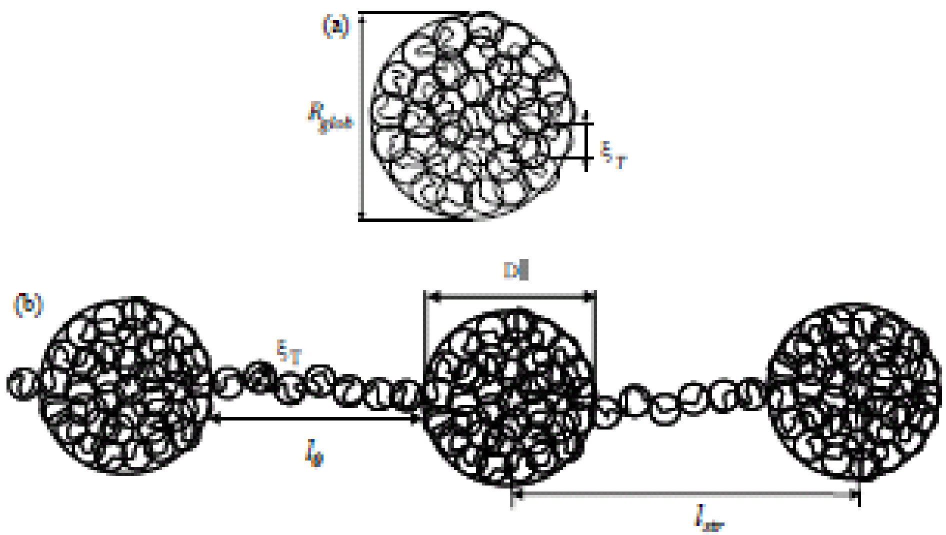
$$\frac{\partial F(R_e)}{\partial R_e} = 0$$

Polyelectrolytes in good or poor solvent

Good solvent, χ<1/2:

$$R_e \approx bNu^{1/3} f^{2/3}\left[\ln\left(eN\left(uf^2\right)^{2/3}\right)\right]^{1/3} \sim N(\ln N)^{1/3} >> N^{1/2}$$

Poor solvent, χ>1/2:



3.7 Thermodynamics of Polymer Mixtures

Why are two kinds of polymers not compatible?

Entropy of Mixing

Polymer/Polymer

$$\Delta S_{x_1N_1,x_2N_2} = -k\left(N_1 \ln \frac{x_1N_1}{x_1N_1 + x_2N_2} + N_2 \ln \frac{x_2N_2}{x_1N_1 + x_2N_2} \right)$$

Solvent/Solvent

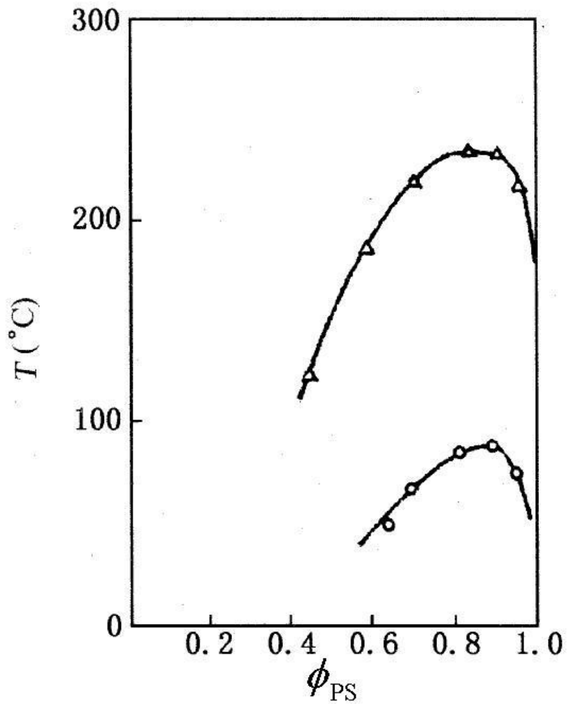
$$\Delta S_{N_1,N_2} = -k\left(N_1 \ln \frac{N_1}{N_1 + N_2} + N_2 \ln \frac{N_2}{N_1 + N_2} \right)$$

Solvent/Solvent

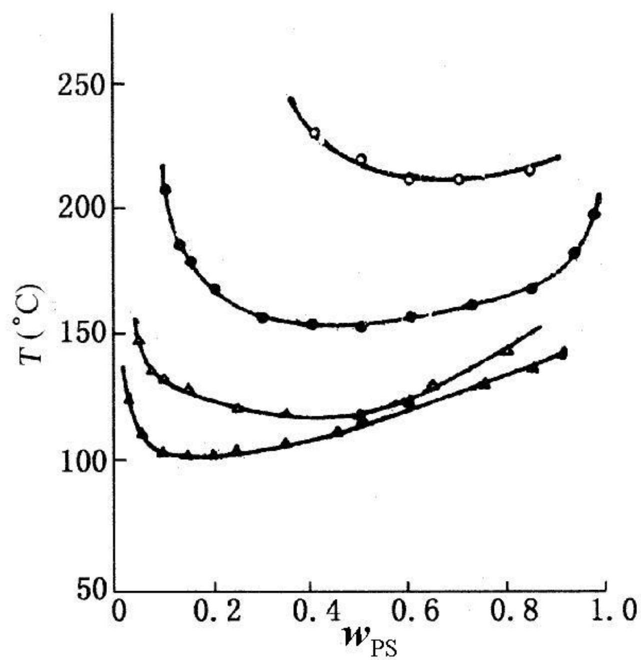
$$\Delta S_{xN_1,xN_2} = -k\left(xN_1 \ln \frac{xN_1}{xN_1 + xN_2} + xN_2 \ln \frac{xN_2}{xN_1 + xN_2} \right)$$

$$\Delta S_{x_1N_1,x_2N_2} \sim \Delta S_{N_1,N_2} << \Delta S_{xN_1,xN_2}$$

Phase Diagram



UCST

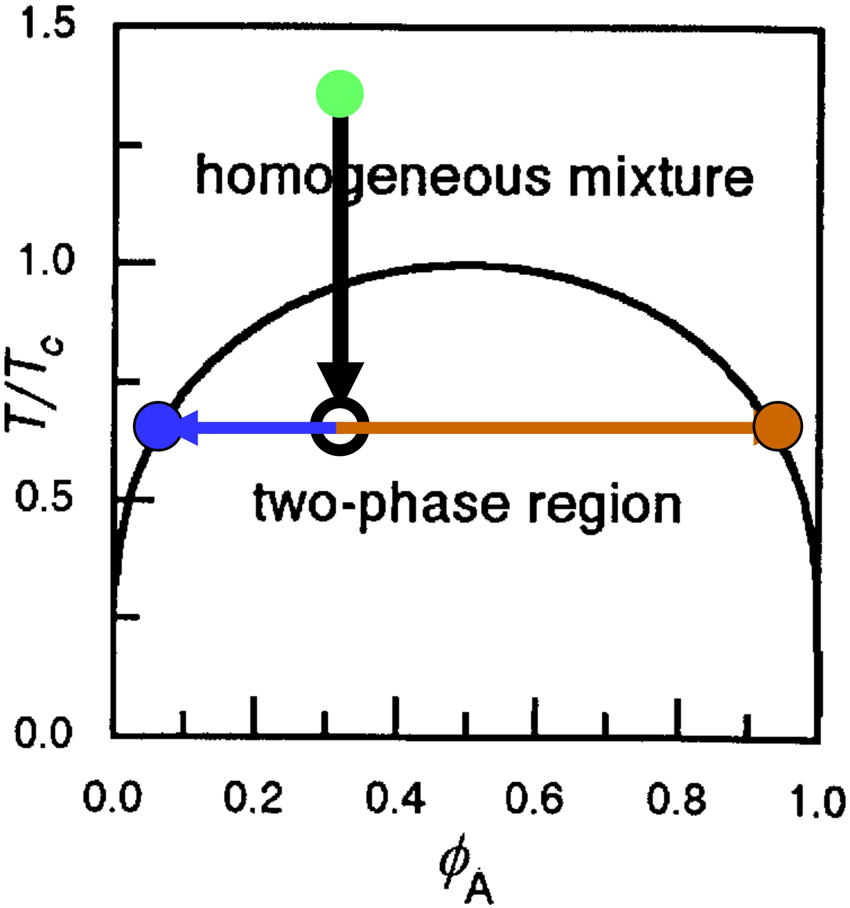


LCST

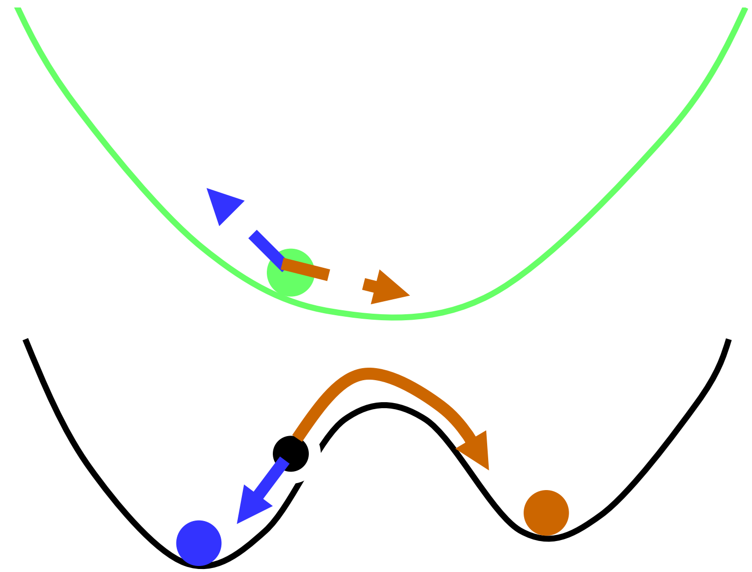
The Phase Behavior of Polymer Mixtures

How to judge it's homogeneous state or inhomogeneous state ?

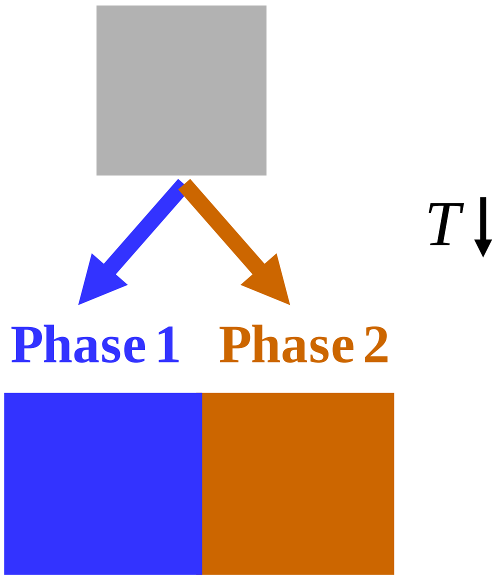
What is the mechanism of phase separation?

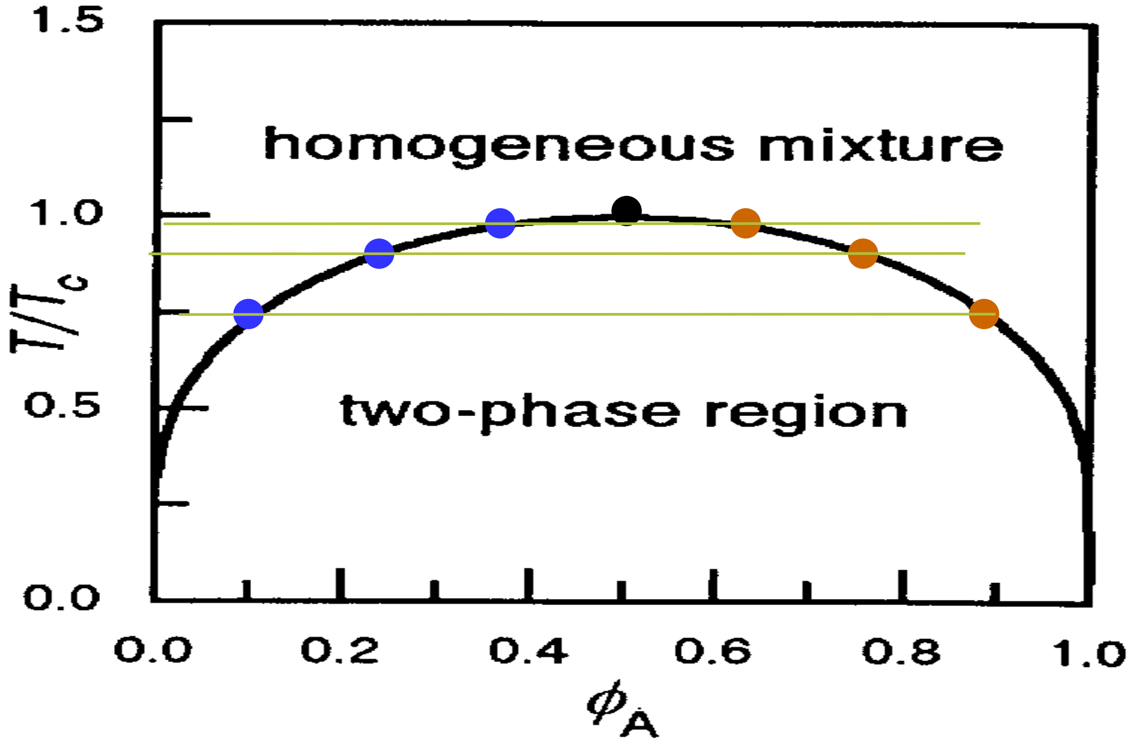


$$V_1\Delta G_1+(1-V_1)\Delta G_2-\Delta G<0$$



Phase Diagram and Phase Equilibrium





$$\left.\begin{aligned}\Delta\mu_1^1 &= \Delta\mu_1^2 \\ \Delta\mu_2^1 &= \Delta\mu_2^2\end{aligned}\right\}$$

$$\phi_1^1 + \phi_2^1 = 1$$

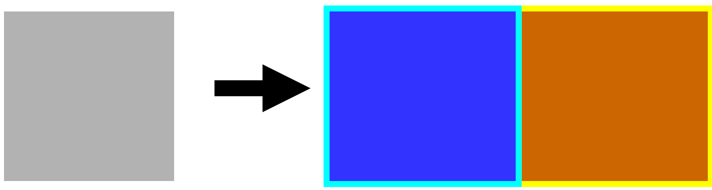
$$\phi_1^2 + \phi_2^2 = 1$$

$$\rightarrow$$

$$\ln\left(1-\phi_2^1\right) + \left(1-\frac{x_1}{x_2}\right)\phi_2^1 + x_1\chi\left(\phi_2^1\right)^2 = \ln\left(1-\phi_2^2\right) + \left(1-\frac{x_1}{x_2}\right)\phi_2^2 + x_1\chi\left(\phi_2^2\right)^2$$

$$\ln\phi_2^1 + \left(1-\frac{x_2}{x_1}\right)\left(1-\phi_2^1\right) + x_2\chi\left(1-\phi_2^1\right)^2 = \ln\phi_2^2 + \left(1-\frac{x_2}{x_1}\right)\left(1-\phi_2^2\right) + x_2\chi\left(1-\phi_2^2\right)^2$$

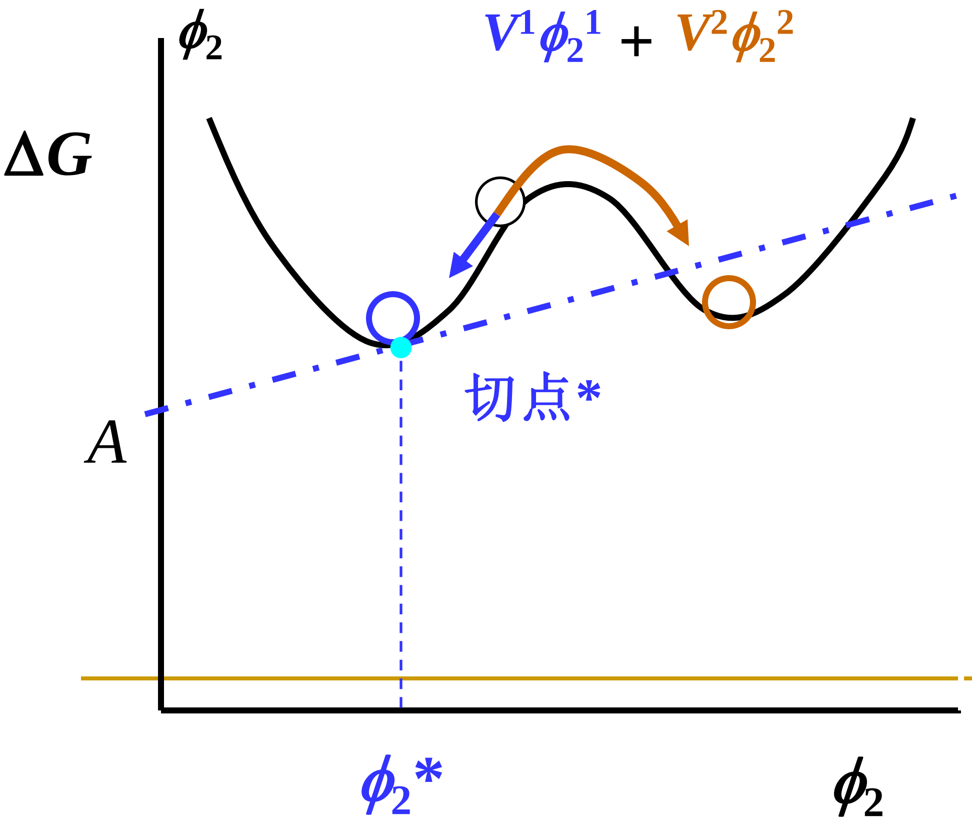
How to calculate the phase diagram from free energy ?



$\Delta\mu_1^1 = \Delta\mu_1^2$

$\Delta\mu_2^1 = \Delta\mu_2^2$

$V^1\phi_2^1 + V^2\phi_2^2$



$$d\Delta G = \Delta\mu_1 dn_1 + \Delta\mu_2 dn_2$$

$$\Delta G = n_1\Delta\mu_1 + n_2\Delta\mu_2$$

$$\phi_1 = \frac{n_1 x_1 V_s}{V_m}, \quad \phi_2 = \frac{n_2 x_2 V_s}{V_m} \quad \phi_1 = 1 - \phi_2$$

$$\Delta G = \phi_1 \frac{V_m}{V_s} x_1^{-1}\Delta\mu_1 + \phi_2 \frac{V_m}{V_s} x_2^{-1}\Delta\mu_2$$

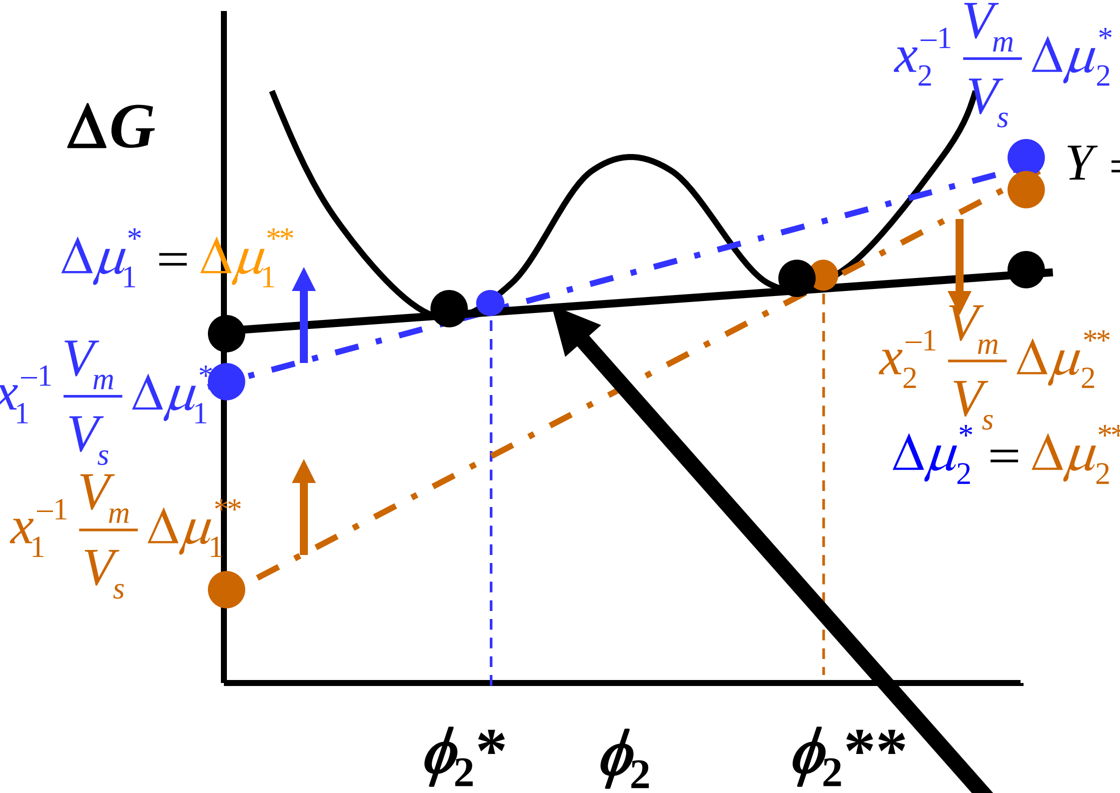
$$= \frac{V_m}{V_s}\left[x_1^{-1}\Delta\mu_1 + \phi_2\left(x_2^{-1}\Delta\mu_2 - x_1^{-1}\Delta\mu_1\right)\right]$$

对ΔG作切线 $Y=A+B\phi_2$, 切点 ϕ_2*

斜率B $B = \left(\frac{\partial \Delta G}{\partial \phi_2}\right)^* = \frac{V_m}{V_s}\left(x_2^{-1}\Delta\mu_2^* - x_1^{-1}\Delta\mu_1^*\right)$

$\Delta G^* = A + B\phi_2^* \longrightarrow A = x_1^{-1}\frac{V_m}{V_s}\Delta\mu_1^*$

Finding the phase equilibrium conditions



$x_2^{-1}\frac{V_m}{V_s}\Delta\mu_2^*$ 对ΔG作的切线方程为

$$Y = x_1^{-1}\frac{V_m}{V_s}\Delta\mu_1^* + \frac{V_m}{V_s}\left(x_2^{-1}\Delta\mu_2^* - x_1^{-1}\Delta\mu_1^*\right)\phi_2$$

$$\phi_2 \to 0, \quad Y_0 = x_1^{-1}\frac{V_m}{V_s}\Delta\mu_1^*$$

$$\phi_2 \to 1, \quad Y_1 = x_2^{-1}\frac{V_m}{V_s}\Delta\mu_2^*$$

要使 $\begin{matrix}\Delta\mu_1^1 = \Delta\mu_1^2 \\ \Delta\mu_2^1 = \Delta\mu_2^2\end{matrix}$ 相平衡条件满足

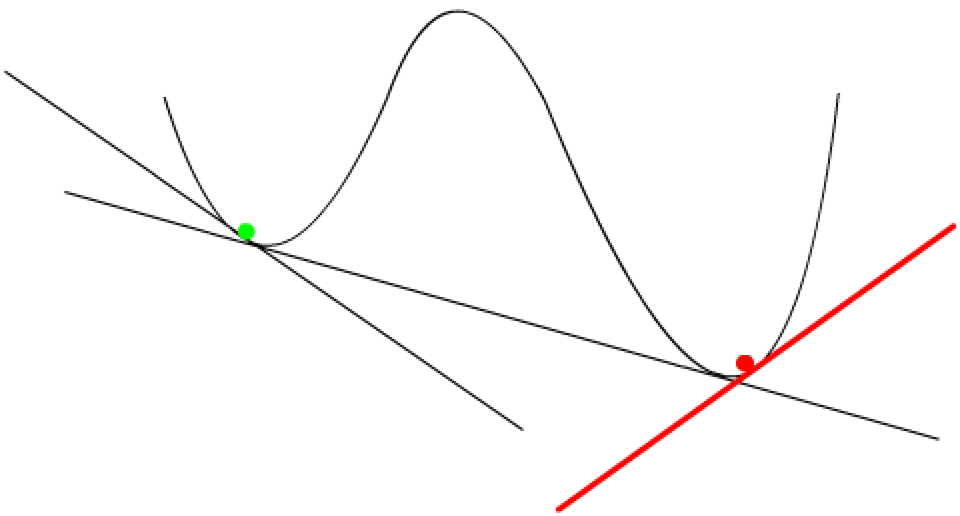
必须作一根这样的切线满足

$$\Delta\mu_1^* = \Delta\mu_1^{**}$$

$$\Delta\mu_2^* = \Delta\mu_2^{**}$$

唯有同时通过两个切点的共切线

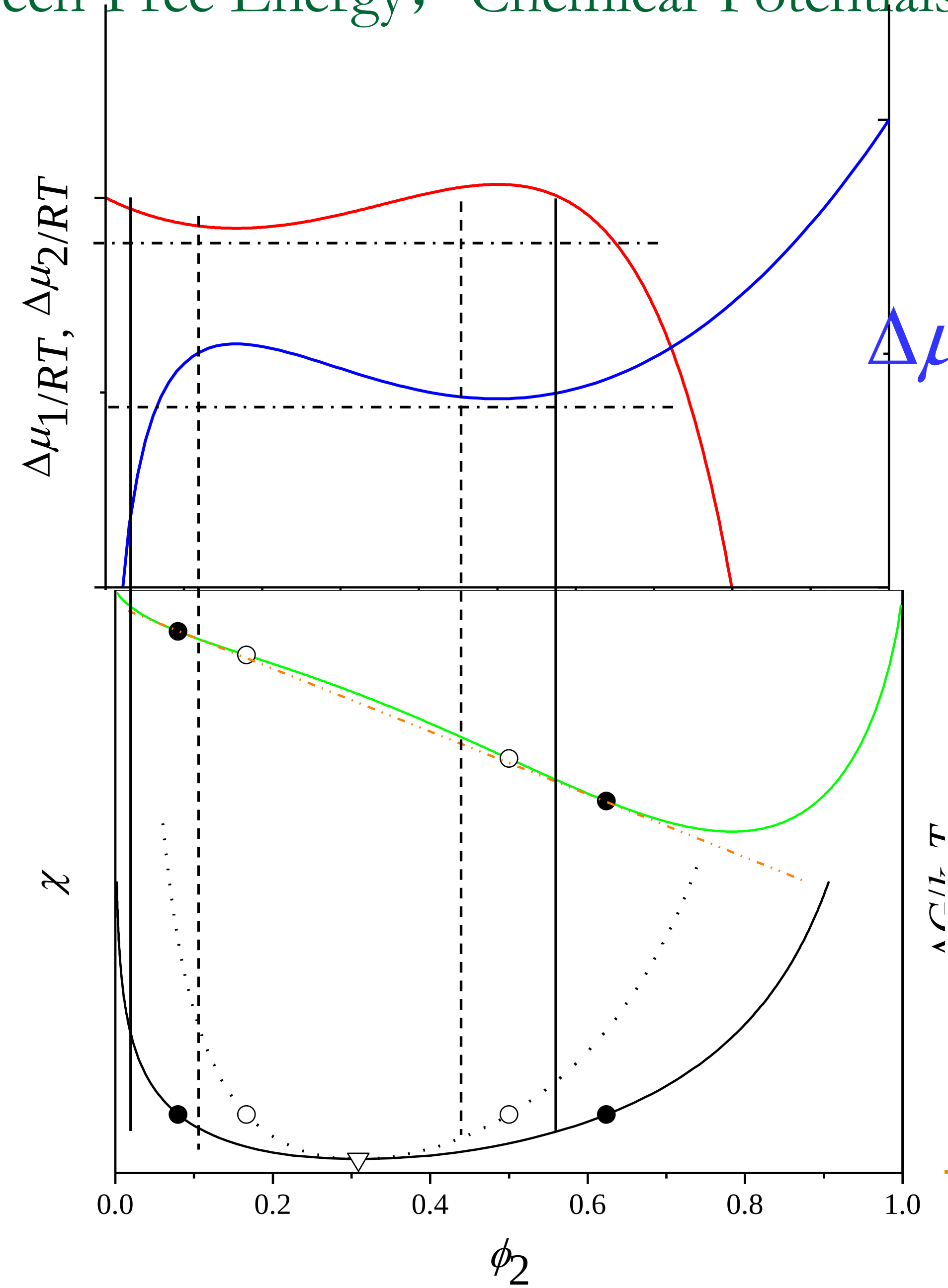
$$\Delta\mu_1^{*} = \Delta\mu_1^{**}$$



$$\Delta\mu_2^{*} = \Delta\mu_2^{**}$$

Relations between Free Energy, Chemical Potentials and Phase Diagram

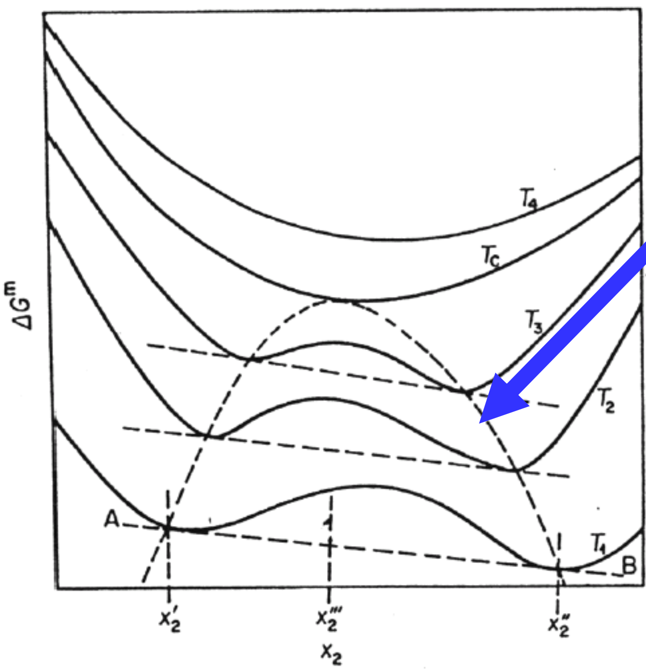
$\Delta\mu_1^{*} = \Delta\mu_1^{**}$

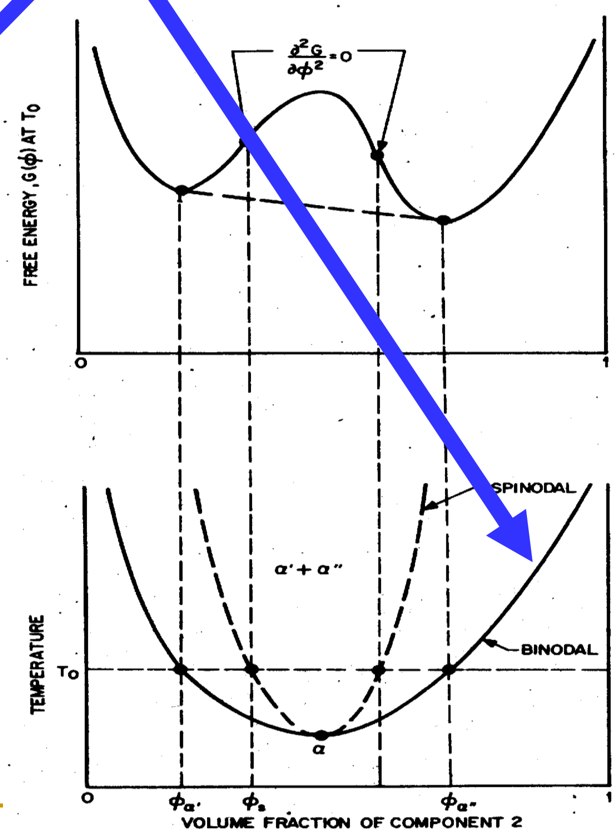


$\Delta\mu_2^{*} = \Delta\mu_2^{**}$

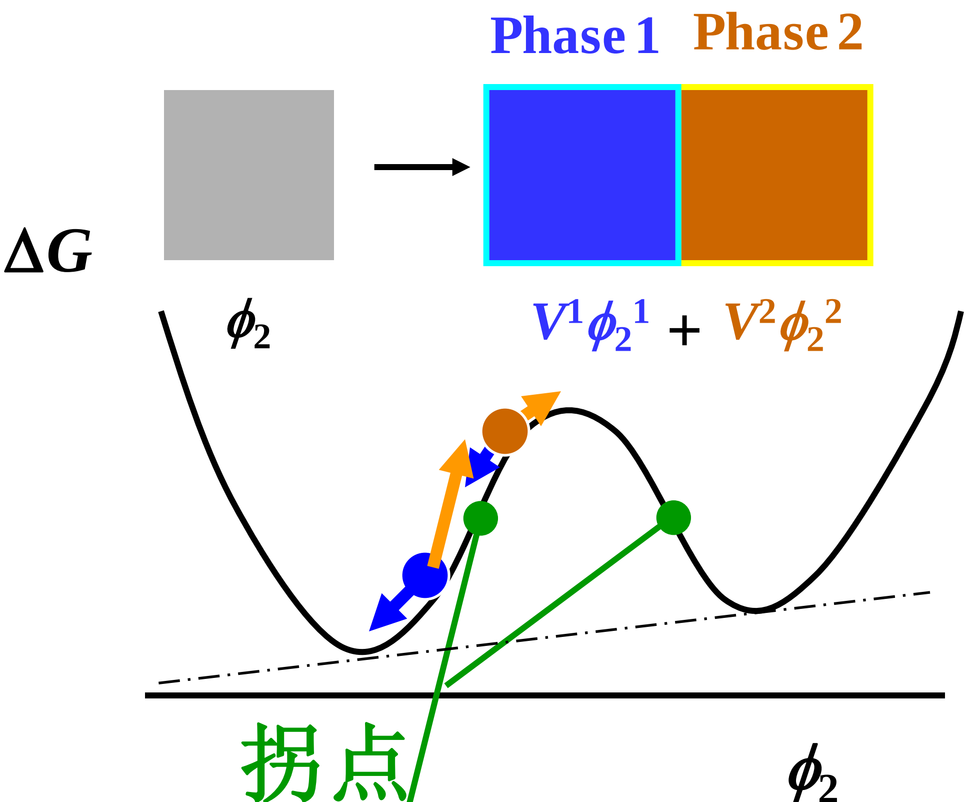
(1) Phase equilibrium curve – binodal

作 $T(\chi) \sim [\phi_2^*(T), \phi_2^{**}(T)]$ ⟶ **binodal curve**

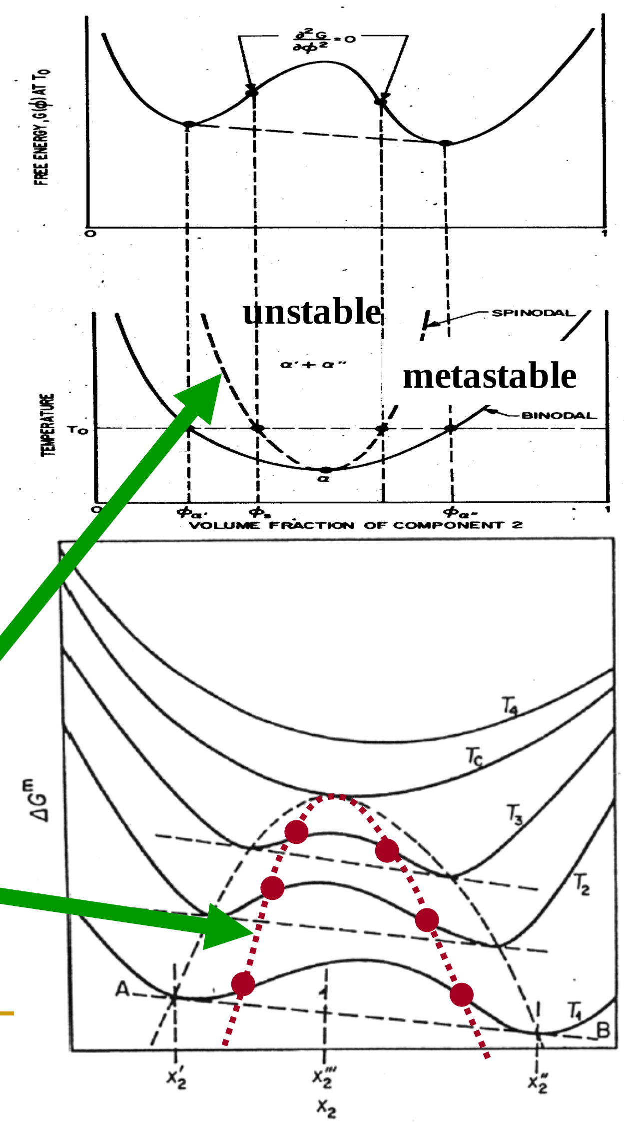




(2) Metastable/unstable limits - spinodal

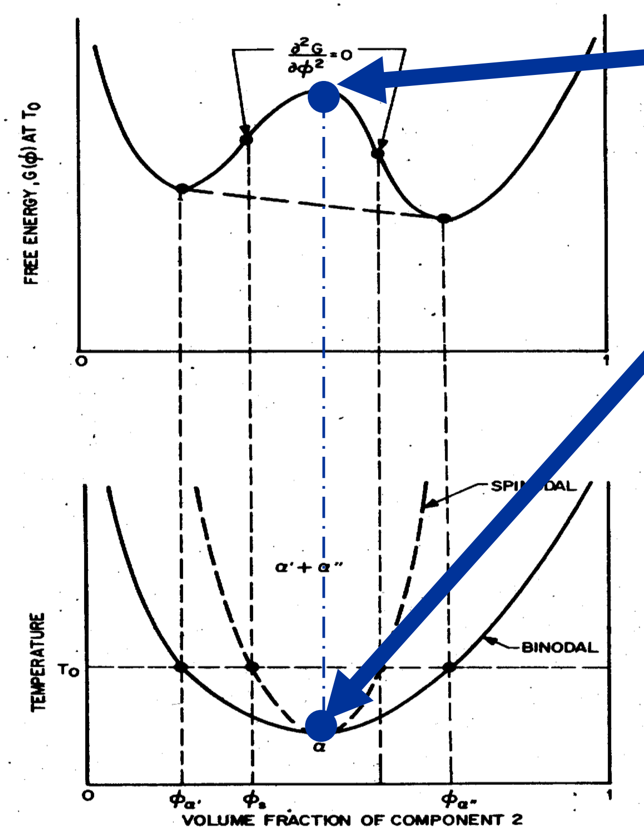


$$\frac{\partial^2 \Delta G}{\partial \phi_2^2} = 0$$ **Spinodal curve**



$$\boxed{\frac{\partial^2 \Delta G}{\partial \phi_2^2} = \frac{1}{x_1\left(1-\phi_2\right)} + \frac{1}{x_2\phi_2} - 2\chi = 0}$$

(3) Critical point



Spinodal 和 binodal的交点: Critical point

$$\frac{\partial^3 \Delta G}{\partial \phi_2^3}=\frac{\partial}{\partial \phi_2}\left[\frac{1}{x_1(1-\phi_2)}+\frac{1}{x_2\phi_2}-2\chi\right]=0$$

$$\boxed{\phi_{2,c}=\frac{x_1^{1/2}}{x_1^{1/2}+x_2^{1/2}},\quad \chi_c=\frac{1}{2}\left(\frac{1}{x_1^{1/2}}+\frac{1}{x_2^{1/2}}\right)^2}$$

For symmetric blends $x_1=x_2$ $\qquad \chi_c N=2$

For polymer solutions $\qquad \chi_c \to \frac{1}{2}$

For symmetric di-blocks $f=0.5$ $\qquad \chi_c N=10.5$

Critical points dependence of *N*

For blends

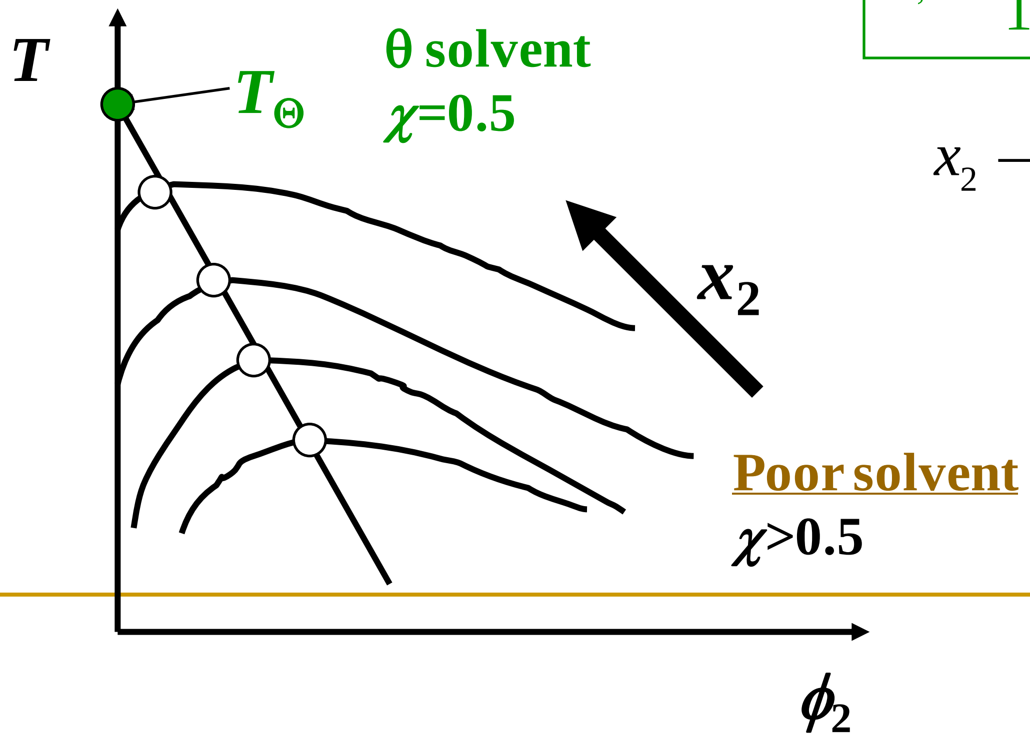
$$\phi_{2,c} = \frac{x_1^{1/2}}{x_1^{1/2} + x_2^{1/2}}, \quad \chi_c = \frac{1}{2}\left(\frac{1}{x_1^{1/2}} + \frac{1}{x_2^{1/2}}\right)^2$$

$$x \uparrow \rightarrow \chi_c \downarrow, \quad T_c \uparrow$$

For solutions

$$\phi_{2,c} = \frac{1}{1 + x_2^{1/2}}, \quad \chi_c = \frac{1}{2}\left(1 + \frac{1}{x_2^{1/2}}\right)^2$$

$$x_2 \rightarrow \infty, \quad \phi_{2c} \rightarrow 0, \quad \chi_c \rightarrow \frac{1}{2}$$

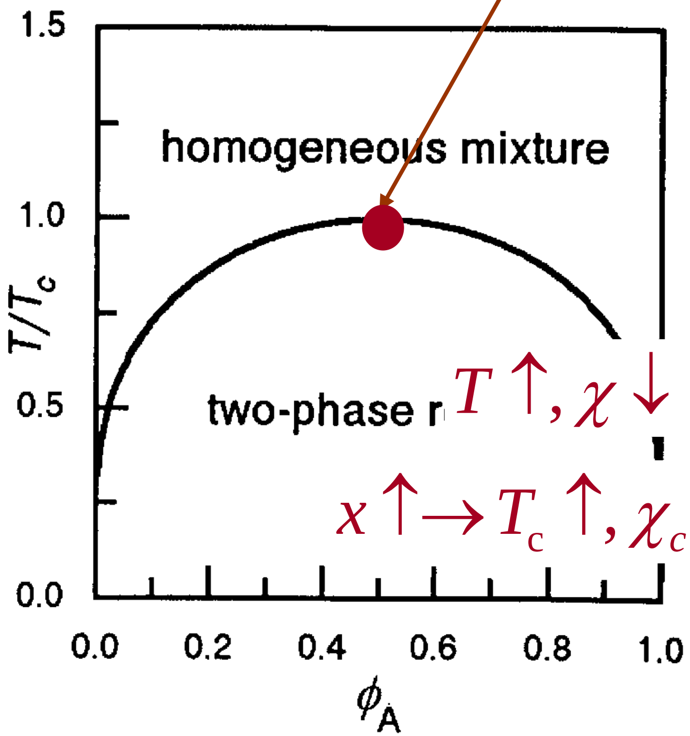


UCST/LCST

$$\chi = \frac{(Z-2)\Delta\varepsilon_{12}}{kT} \qquad \Delta G = \chi\phi_1\phi_2 - T\Delta S$$

Upper critical solution temperature (UCST)

$$\Delta\varepsilon_{12} > 0$$



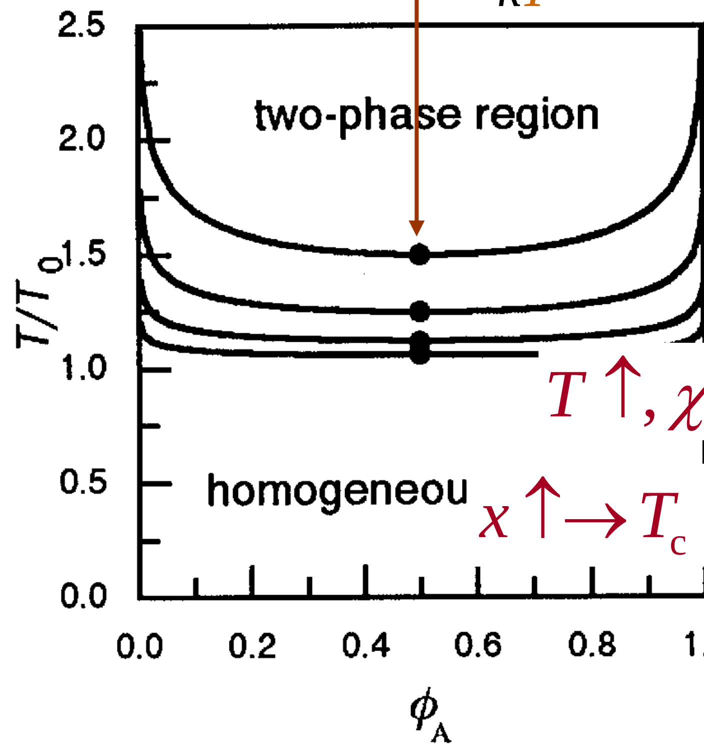
$T\uparrow, \chi\downarrow$

$x\uparrow \rightarrow T_c\uparrow, \chi_c\downarrow$

Endothermic symmetrical polymer mixture with lower miscibility gap.

Lower critical solution temperature (LCST)

$$\Delta\varepsilon_{12} < 0 \qquad \chi = \frac{(Z-2)\Delta\varepsilon_{12}}{kT} + B \quad B > 0$$



$T\uparrow, \chi\uparrow$

$x\uparrow \rightarrow T_c\downarrow, \chi_c\downarrow$

Exothermal symmetrical polymer mixture with upper miscibility gap.

Why UCST or LCST

$$\Delta G_{mix} = RTV\left(\frac{\phi_A}{N_A}\ln\phi_A + \frac{\phi_B}{N_B}\ln\phi_B + \chi\phi_A\phi_B\right) \longrightarrow$$

χ is the key issue.

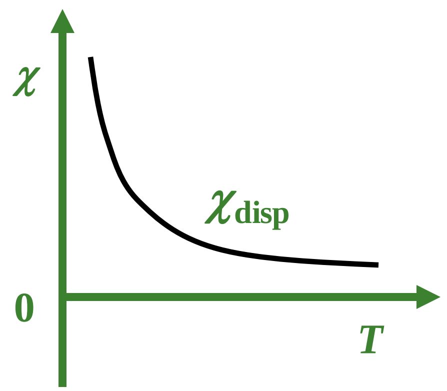
➢ **Effective interaction parameter χ_{eff}:**

Dispersion forces

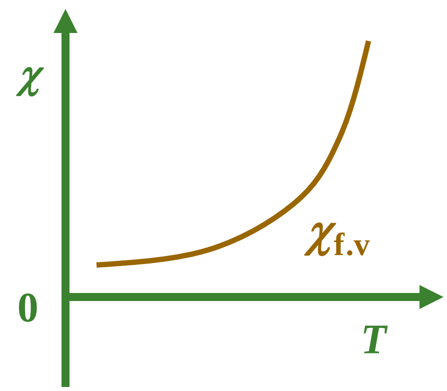
Free volume effects $\longrightarrow$ $\chi_{\text{eff}} = \chi_{\text{disp}} + \chi_{\text{f.v.}} + \chi_{\text{s.i.}} = \frac{A}{T} + B$

Specific interactions

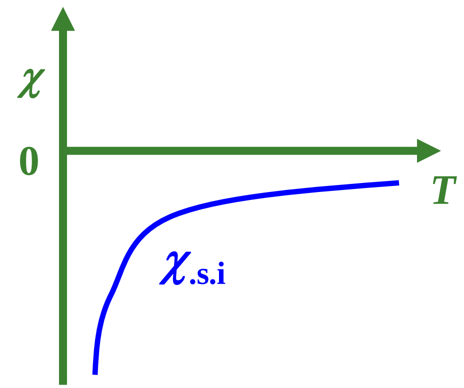
***A*>0 UCST**
***A*<0 LCST**



Dispersion force:
~1/*T* monotonic decreasing,
$\chi_{\text{disp}} \rightarrow 0$ as $T \rightarrow \infty$.



Free volume effect:
Monotonic increasing with *T*,
small, but positive at low *T*.



Specific interaction:
Always < 0, decreasing
magnitude with increasing *T*.

Phase Equilibrium

1. 相平衡线

在某一温度下,达到热力学平衡的两相平衡点

(1)自由能曲线作共切线取两切点法

(2)数值解

$$\Delta\mu_1^1 = \Delta\mu_1^2 \qquad \phi_1^1 + \phi_2^1 = 1$$

$$\Delta\mu_2^1 = \Delta\mu_2^2 \qquad \phi_1^2 + \phi_2^2 = 1$$

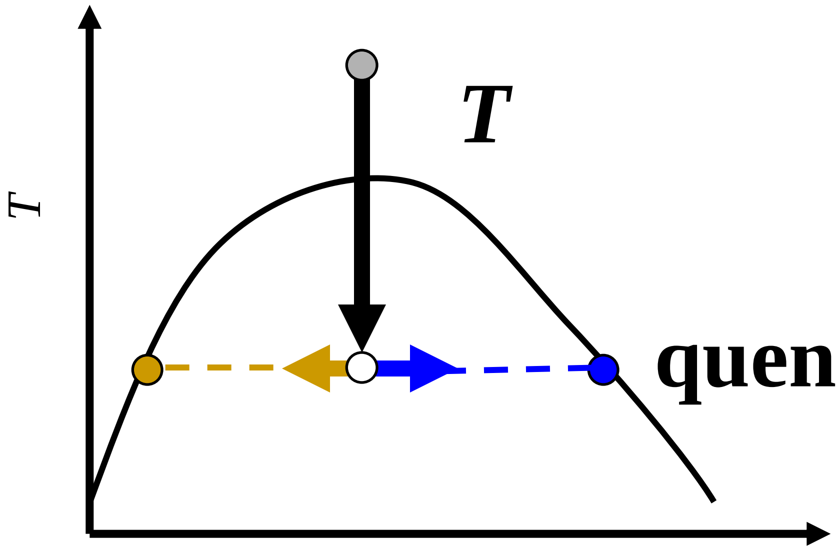
$$\ln\phi_1^1 + \left(1 - \frac{x_1}{x_2}\right)\phi_2^1 + x_1\chi\left(\phi_2^1\right)^2 = \ln\phi_1^2 + \left(1 - \frac{x_1}{x_2}\right)\phi_2^2 + x_1\chi\left(\phi_2^2\right)^2$$

$$\ln\phi_2^1 + \left(1 - \frac{x_2}{x_1}\right)\phi_1^1 + x_2\chi\left(\phi_1^1\right)^2 = \ln\phi_2^2 + \left(1 - \frac{x_2}{x_1}\right)\phi_1^2 + x_2\chi\left(\phi_1^2\right)^2$$

2. spinodal线

与相分离机理和动力学有关

Phase Separation Dynamics



quenching(淬火)

达到两相最终平衡的动力学过程

与初始状态的浓度有关

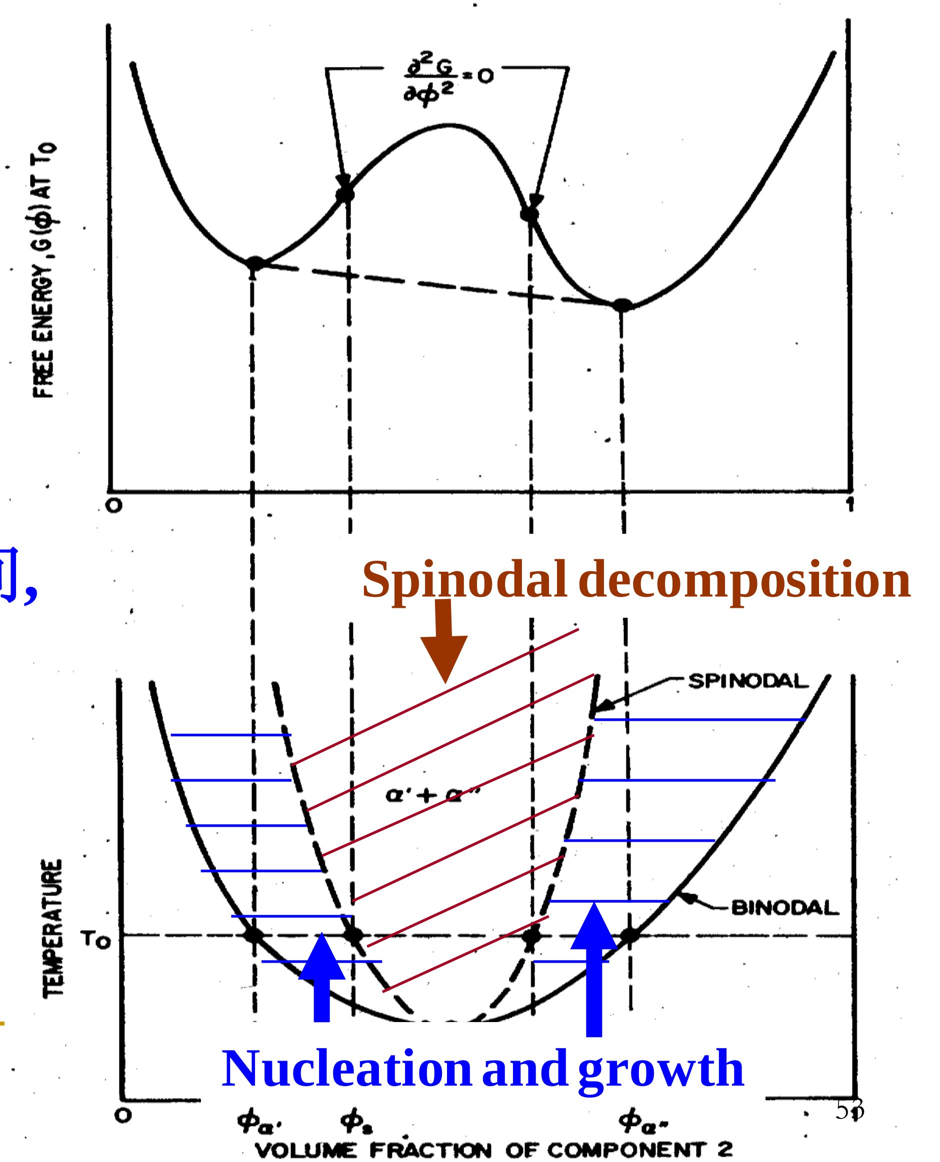
(1) 在临界组成附近，不稳区，spinodal decomposition

(2) 在相平衡线和spinodal线之间，亚稳区，nucleation and growth

Phase diagram and phase separation mechanisms

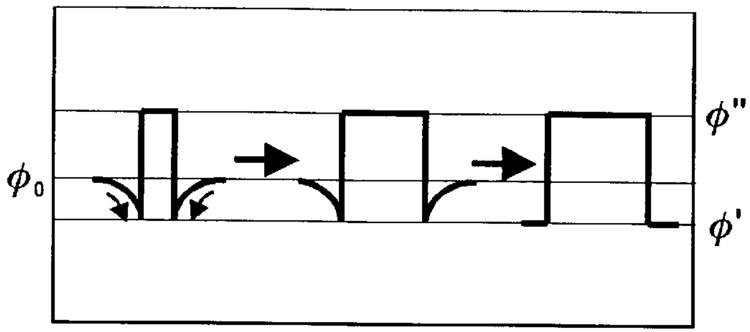
(1) 在临界组成附近,不稳区, spinodal decomposition

(2) 在相平衡线和spinodal线之间, 亚稳区, nucleation and growth



Phase Separation Mechanisms

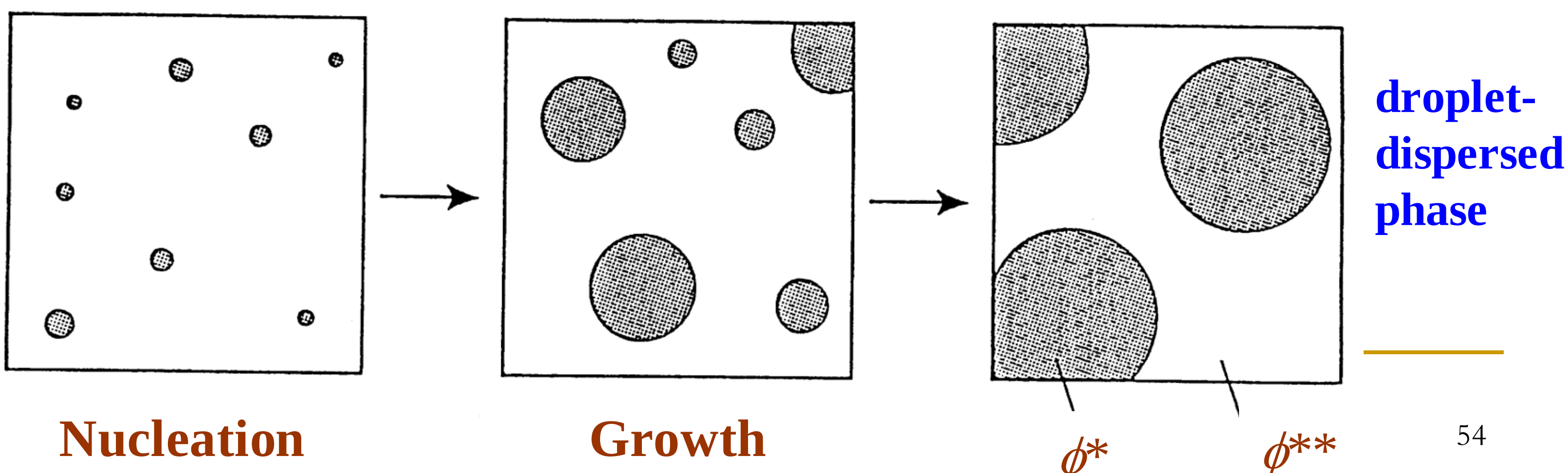
1. Nucleation and growth (成核生长) mechanism



In metastable region, separation can proceed only by overcoming the barrier with a large fluctuation in composition.

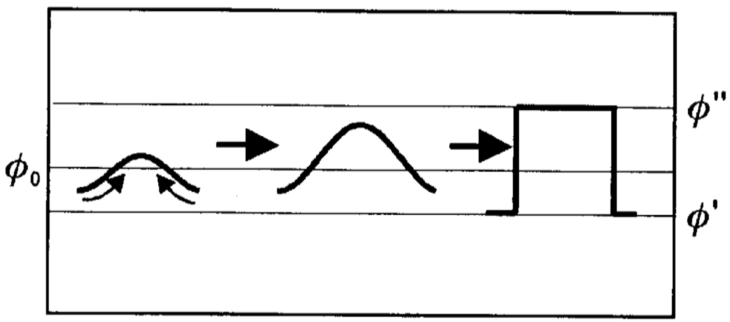
Nucleation barrier: $\Delta G(r) = -\frac{4\pi}{3} r^3 \Delta g + 4\pi r^2 \sigma$ with $\Delta g = g(\phi_0) - g(\phi'')$

r: radius of the nuclear; *σ*: excess free energy per unit surface area.



Phase Separation Mechanisms

2. Spinodal decomposition (亚稳极限分解) mechanism

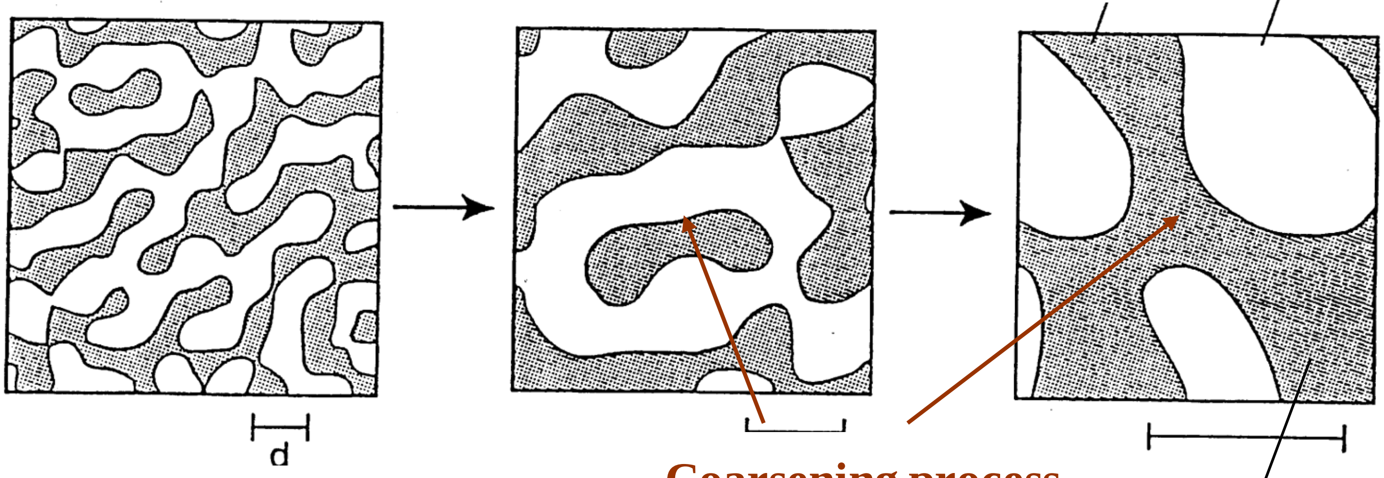


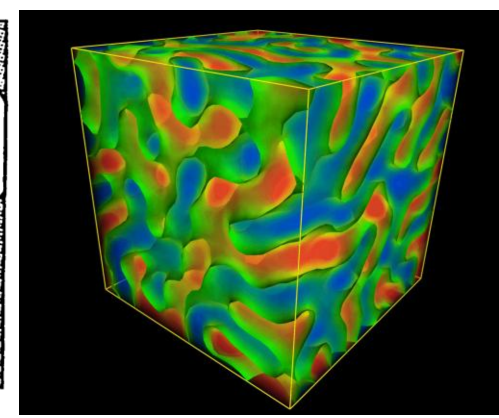
In unstable region, separation can occur spontaneously and continuously without any thermodynamic barrier.

Early stage
No sharp interface

Late stage
Well-established interfaces

ϕ^{**}



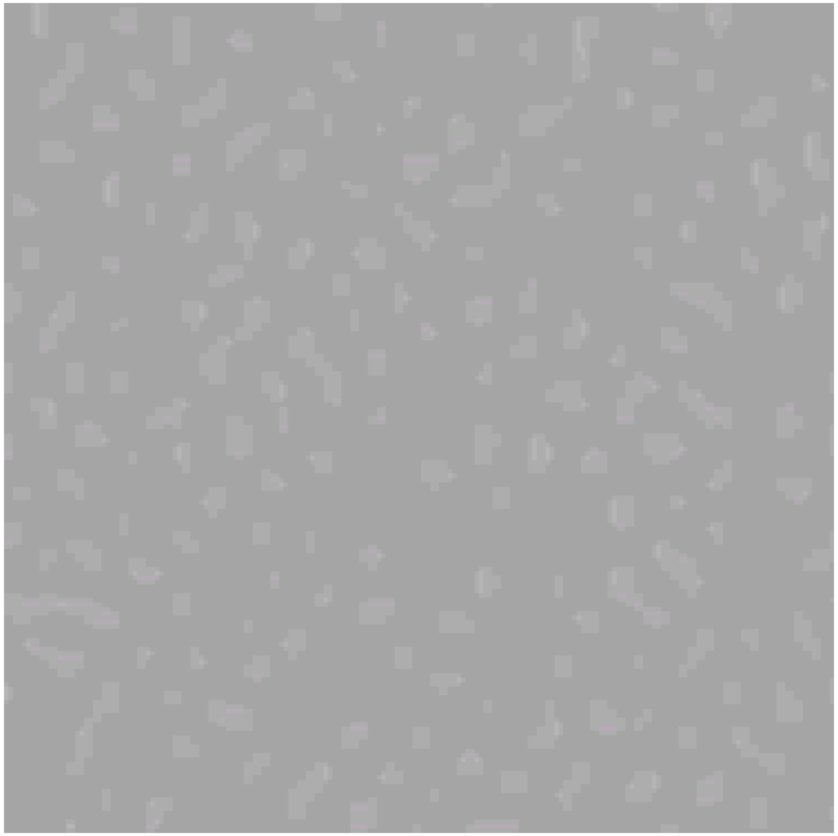


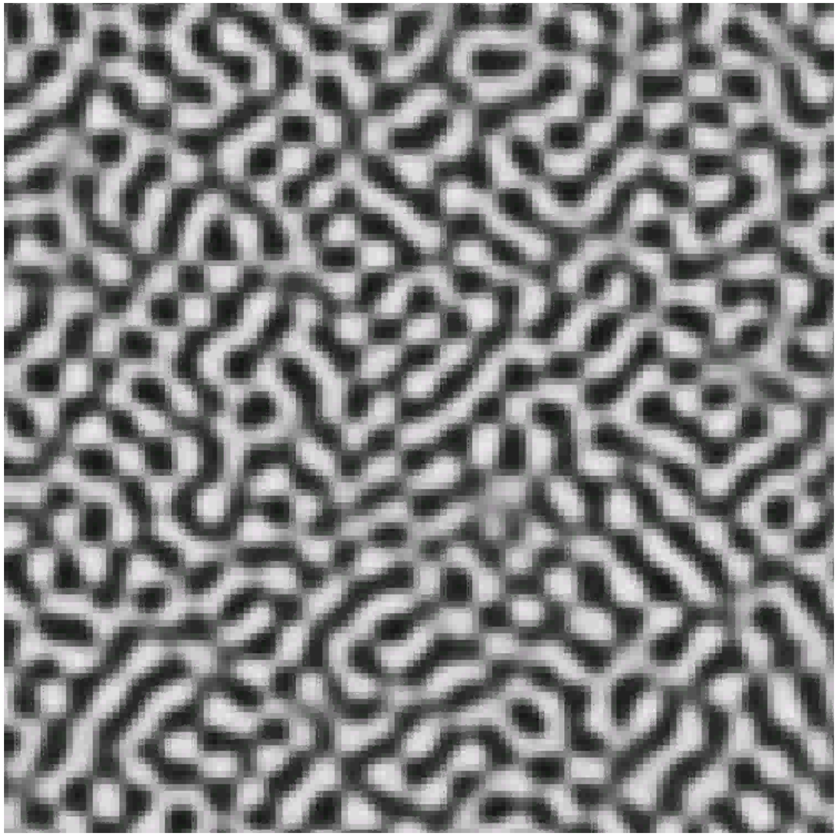
Coarsening process

ϕ^{*}

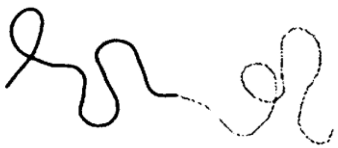
Co/bi-continuous phase

Examples of Phase Separation Dynamics

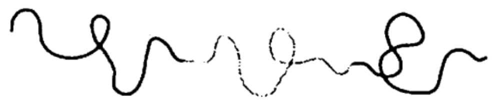




3.8 Theromodynamics of Block Copolymers

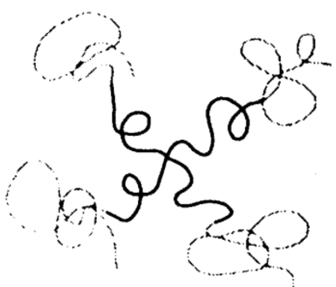


diblock

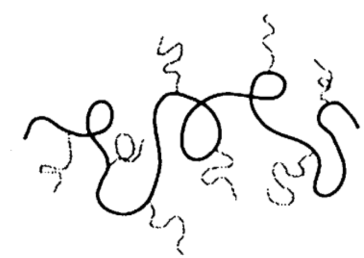


triblock

random multiblock



four arm starblock

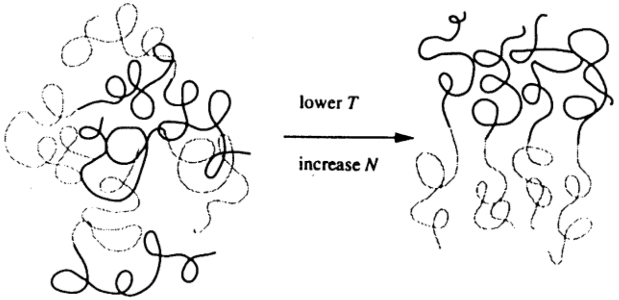


graft copolymer

Self-assembly of Diblock Copolymers

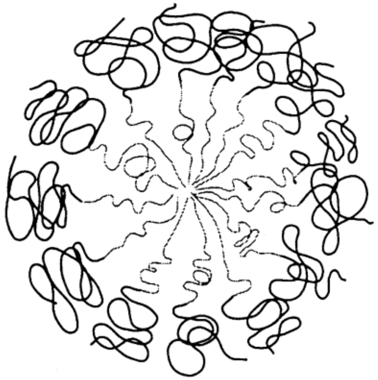
➢ Melts

Microphase (mesophase, nanophase) separation (微相分离) is driven by chemical incompatibilities between the different blocks that make up block copolymer molecules.



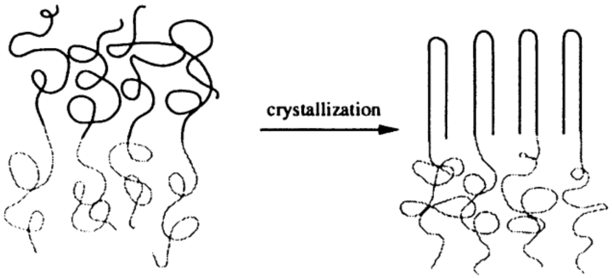
➢ Solutions

Micellization (胶束化) occurs when block copolymer chains associate into, often spherical, micelles (胶束) in dilute solution in a selective solvent (选择性溶剂). In concentrated solution, micelles can order into gels (凝胶).



➢ Solids

Crystallization of the crystalline block from melt often leads to a distinct (usually lamellar (片晶)) structure, with a different periodicity from the melt .



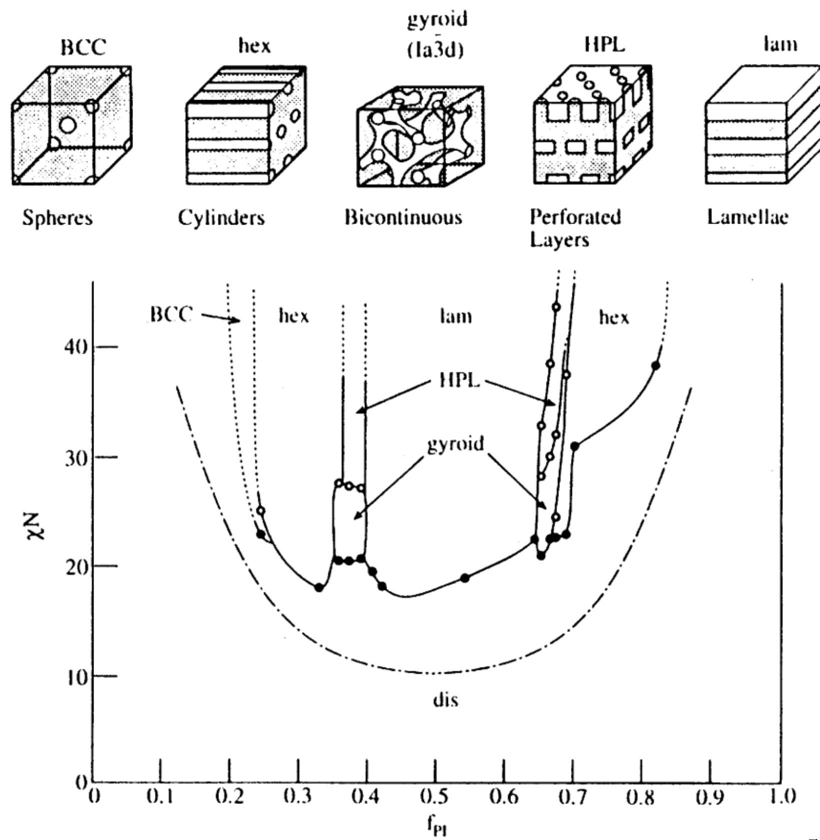
Microphase Separation of Diblock Copolymers (BCPs)

➢ Phase diagram

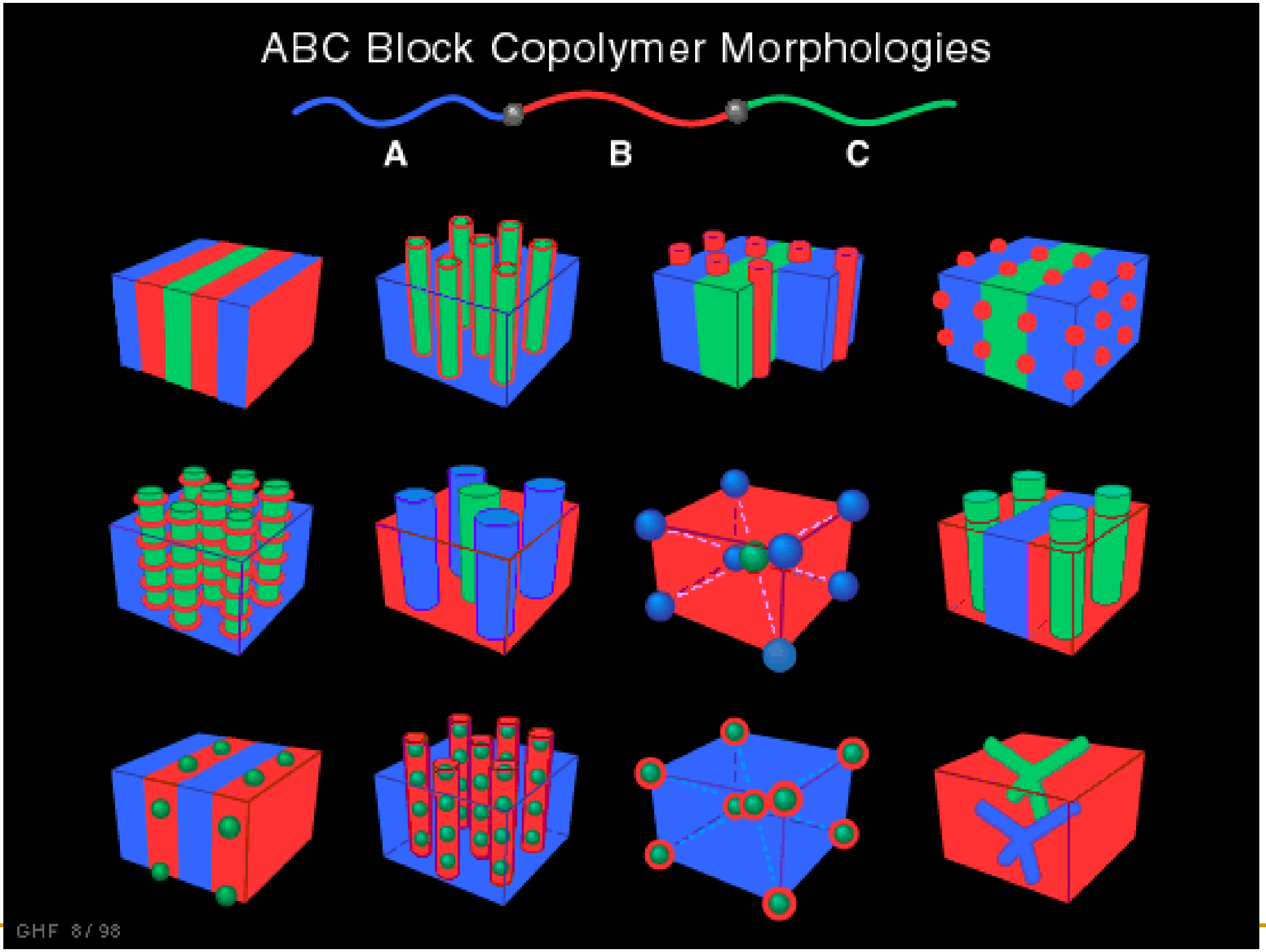
Homogeneous State $\xrightarrow[\text{disorder}]{\text{order}}$ Structurally Order State $\xrightarrow[\text{order}]{\text{order}}$ Structurally Order State

- ➢ *f* is the volume fraction of one component. *f* controls which ordered structures are accessed beneath the order-disorder transition.

- ➢ *χN* expresses the enthalpic-entropic balance. It is used to parameterize block copolymer phase behavior, along with the composition of the copolymer.

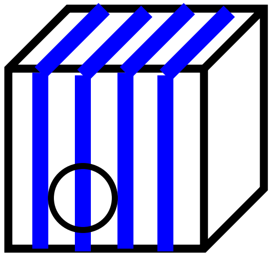


Microphase Separation of Triblock Copolymers

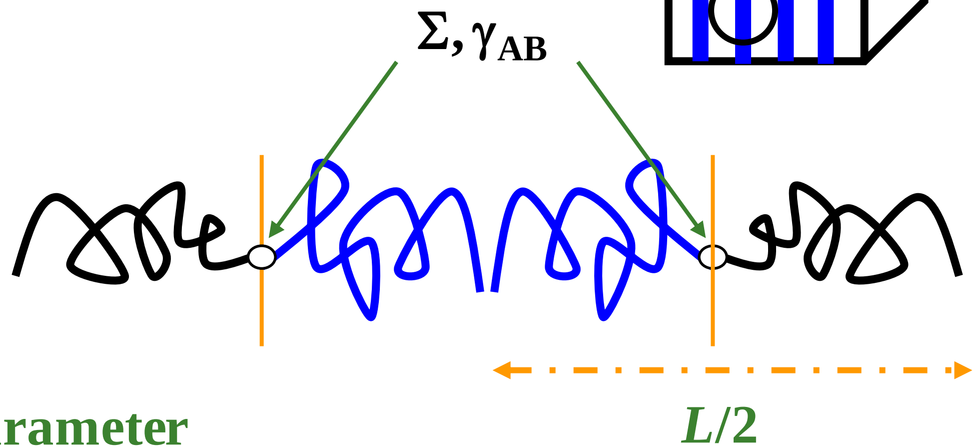


Thermodynamics of Microphase Separation

- **Minimize interfacial area and Maximize chain conformational entropy (MIN-MAX Principle)**



F: free energy per chain
N: number of segments ($=N_A + N_B$)
a: Kuhn length $v_a \sim a^3$, $a_A \sim a_B$
L: domain periodicity
Σ: interfacial area per chain
γ_{AB}: interfacial energy per area
χ_{AB}: segment-segment interaction parameter



Lamellar structure

$$\gamma_{AB} = \frac{kT}{a^2}\sqrt{\frac{\chi_{AB}}{6}}$$

(Helfand, E.; Tagami, Y. ***Polymer Letters***, **1971**, *9*, 741)

$$\chi_{AB} = \frac{Z-2}{kT}\left(\varepsilon_{AB} - \frac{1}{2}(\varepsilon_{AA} - \varepsilon_{BB})\right) \quad \textbf{and} \quad \chi_{AB} \sim \frac{A}{T} + B$$

Thermodynamics of Microphase Separation

- **Free energy of lamellae:** $F_{LAM} = \gamma_{AB}\Sigma + \frac{3}{2}kT\frac{(L/2)^2}{Na^2}$ See Appendix

$$F_{LAM} = \underbrace{\gamma_{AB}\Sigma}_{\text{enthalpic term}} + \underbrace{\frac{3}{2}kT\frac{(L/2)^2}{Na^2}}_{\text{entropic spring term}}$$

Using $Na^3 = V = \frac{L}{2}\Sigma$

we have $F_{LAM} = \frac{kT}{a^2}\sqrt{\frac{\chi_{AB}}{6}}\frac{Na^3}{(L/2)} + \frac{3}{2}kT\frac{(L/2)^2}{Na^2} = \frac{\alpha}{L} + L^2\beta$

$$\frac{\partial F_{LAM}}{\partial L} = 0 \longrightarrow -\frac{\alpha}{L_{opt}{}^2} + 2L_{opt}\beta = 0$$

Thus, the optimum period of the lamellae and the lamellar free energy are:

$$\boxed{L_{opt} = \sqrt[3]{\frac{\alpha}{2\beta}} \cong aN^{2/3}\chi_{AB}^{1/6}}$$ **and** $$F_{LAM}(L_{opt}) = \frac{\alpha}{L_{opt}} + L_{opt}^2\beta \qquad F_{LAM} \cong 1.2kTN^{1/3}\chi_{AB}^{1/3}$$

Assume $F_{disorder} \approx \frac{\widetilde{V_m}}{\widetilde{V_s}}\chi_{AB}\phi_A\phi_B kT = N\chi_{AB}\phi_A\phi_B kT$

At the order-disorder transition: $F_{LAM} = F_{disordered}$

For a 50/50 volume fraction, $\phi_A\phi_B$ =1/4, so: $1.2kTN^{1/3}\chi_{AB}^{1/3} = \frac{1}{4}N\chi_{AB}kT$

BCPs $\boxed{(\chi N)_c = (4.8)^{3/2} \sim 10.5}$ **Critical point** **Symmetric blends** $\boxed{\chi_c N = 2}$

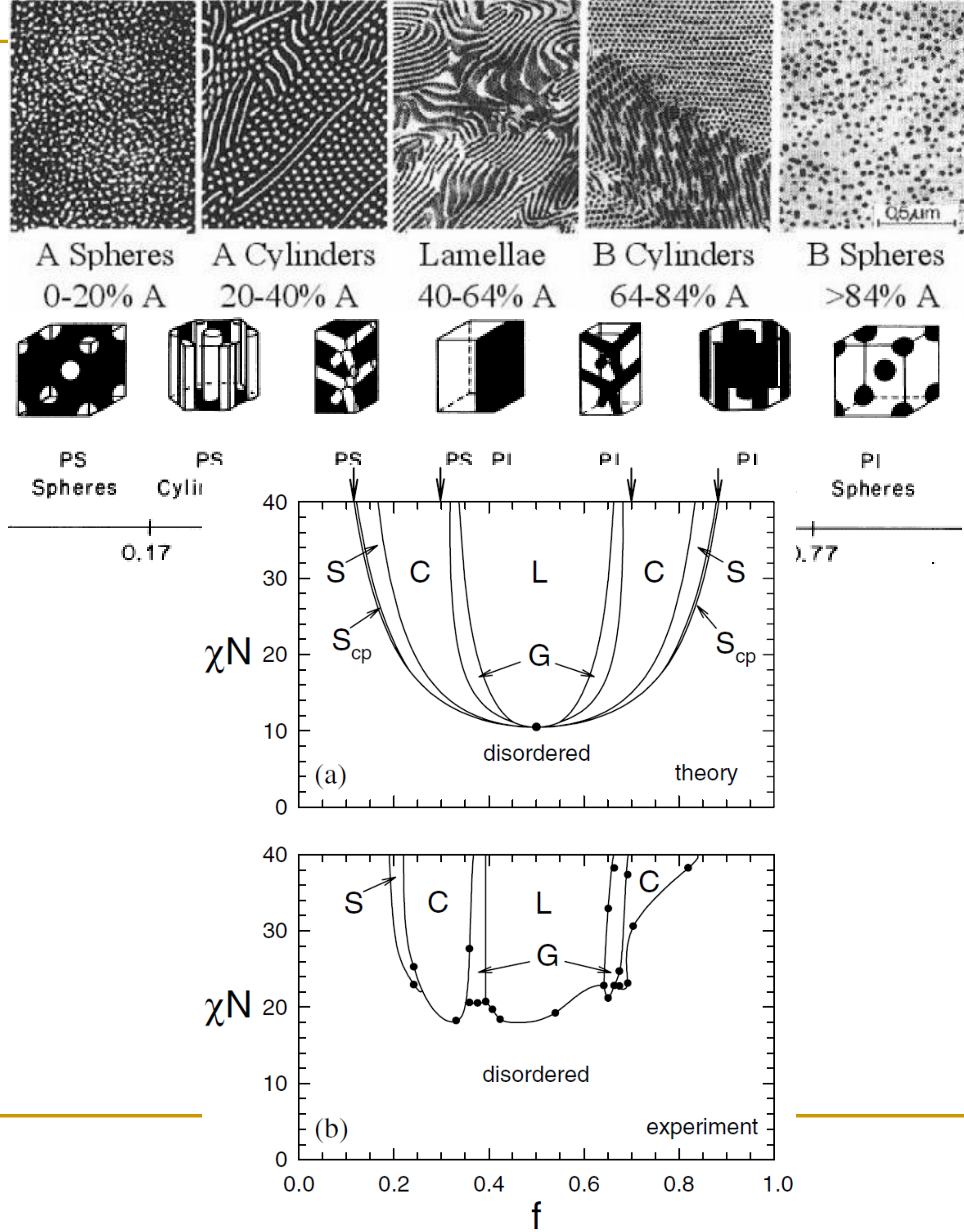
Appendix

$$S_{el}(h) = k\ln\Omega = k\ln\Phi\left(h,N\right) = k\ln\left[\left(\frac{3}{2\pi Na^2}\right)^{3/2}\exp\left(-\frac{3h^2}{2Na^2}\right)\right]$$

$$= k\ln\left(\frac{3}{2\pi Na^2}\right)^{3/2} + k\ln\left[\exp\left(-\frac{3h^2}{2Na^2}\right)\right]$$

$$= -k\,\frac{3h^2}{2Na^2} + const.$$

$$F_{el}(h = L/2) = \frac{3}{2}kT\,\frac{\left(L/2\right)^2 - Na^2}{Na^2} = \frac{3}{2}kT\left(\frac{\left(L/2\right)^2}{Na^2} - 1\right) \approx \frac{3}{2}kT\,\frac{\left(L/2\right)^2}{Na^2}$$


A Spheres
0-20% A
A Cylinders
20-40% A
Lamellae
40-64% A
B Cylinders
64-84% A
B Spheres
>84% A
0.5 μm
PS
Spheres
PS
PI
Spheres
0.17
S
C
L
C
S
S
cp
G
disordered
(a)
theory
χN
S
C
L
C
G
disordered
(b)
experiment
χN
f

χ - the key parameter in polymer physics

(1) 溶液中链的构象

(2) 凝胶的体积相变

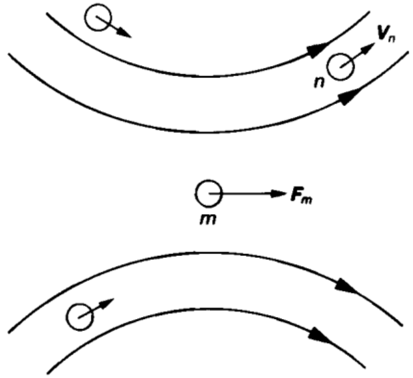
(3) 高分子溶液和共混物的相平衡

(4) 高分子溶液和共混物的相分离

(5) 高分子嵌段共聚物的微相分离

…

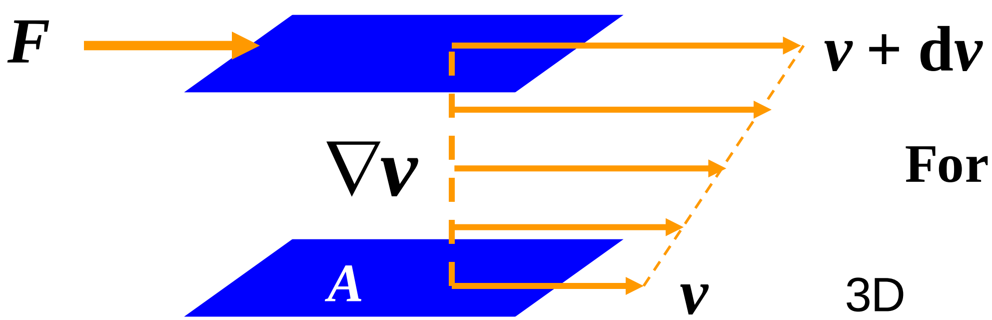
3.9 Hydrodynamics Properties of Polymer Solutions



$$\boldsymbol{v}(\boldsymbol{r}) = \sum_m \boldsymbol{H}_{nm} \cdot \boldsymbol{F}_m$$

$$\boldsymbol{v}(\boldsymbol{r}) = \int d\boldsymbol{r}' H(\boldsymbol{r}-\boldsymbol{r}') \cdot g(\boldsymbol{r}')$$

Correlation function: $\boldsymbol{H}_{nm}$ or $\boldsymbol{H}(\boldsymbol{r}-\boldsymbol{r}')$



For Newtonian fluids

3D $\quad \dfrac{\boldsymbol{F}}{A} = \boldsymbol{\sigma} = \eta\left[\nabla\boldsymbol{v} + (\nabla\boldsymbol{v})^T\right]$

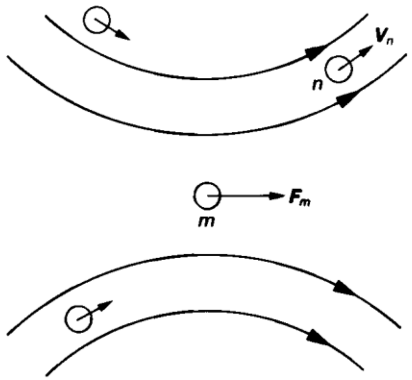
2D $\quad \boldsymbol{\sigma} = \eta \dfrac{\mathrm{d}\boldsymbol{v}}{\mathrm{d}y}$

Velocity and Oseen Tensor

The Momentum Equation – Navier-Stokes Equation

$$\rho \frac{\partial \boldsymbol{v}}{\partial t} = \eta \nabla \cdot \boldsymbol{\sigma} + \nabla P + g(\boldsymbol{r}) = \eta \nabla^2 \boldsymbol{v} + \nabla P + g(\boldsymbol{r})$$

$$\nabla \cdot \boldsymbol{v} = 0$$



Stokes Approximation:

$$\eta \nabla^2 \boldsymbol{v} + \nabla P = -g(\boldsymbol{r})$$

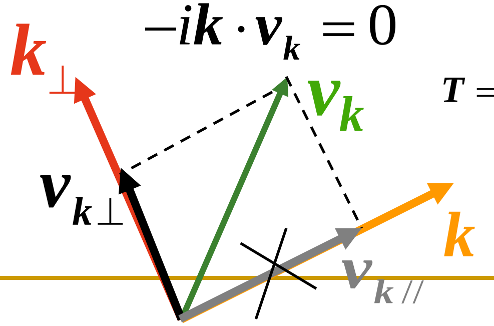
$$\nabla \cdot \boldsymbol{v} = 0$$

In Fourier Space: $\nabla \to -ik$ $\quad \nabla^2 \to (-ik)^2$

$$-\eta \boldsymbol{k}^2 \boldsymbol{v}_{\boldsymbol{k}} - i\boldsymbol{k} P_{\boldsymbol{k}} = -g_{\boldsymbol{k}}$$

$$-i\boldsymbol{k} \cdot \boldsymbol{v}_{\boldsymbol{k}} = 0$$

$$\left(-\eta \boldsymbol{k}^2 \boldsymbol{v}_{\boldsymbol{k}} + g_{\boldsymbol{k}}\right)_{\perp} = 0$$



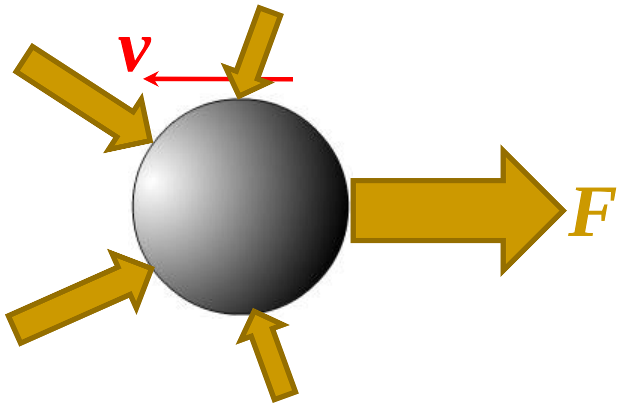
$$\boldsymbol{T} = \left(\boldsymbol{I} - \hat{\boldsymbol{k}}\hat{\boldsymbol{k}}\right)$$

$$v_{\boldsymbol{k}} = \frac{1}{\eta \boldsymbol{k}^2}\left(\boldsymbol{I} - \hat{\boldsymbol{k}}\hat{\boldsymbol{k}}\right) \cdot g_{\boldsymbol{k}} = \boldsymbol{H}(\boldsymbol{k}) \cdot g_{\boldsymbol{k}}$$

$$\boldsymbol{v}(\boldsymbol{r}) = \int d\boldsymbol{r}'\, H(\boldsymbol{r} - \boldsymbol{r}') \cdot g(\boldsymbol{r}')$$

$$\boxed{\boldsymbol{H}(\boldsymbol{r}) = \frac{1}{(2\pi)^3} \int d\boldsymbol{k}\, \frac{1}{\eta \boldsymbol{k}^2}\left(\boldsymbol{I} - \hat{\boldsymbol{k}}\hat{\boldsymbol{k}}\right) e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} = \frac{1}{8\pi\eta r}\left(\boldsymbol{I} + \hat{\boldsymbol{r}}\hat{\boldsymbol{r}}\right)}$$

Diffusion of Suspensions in Solution



Stokes formula

$$\boldsymbol{F} = -6\pi R\eta \boldsymbol{v} = -\zeta \boldsymbol{v}$$

Stokes-Einstein relation

$$D = k_B T / \zeta = \frac{k_B T}{6\pi\eta R}$$

$$D = D_0\left(1 + k_D c + \ldots\right)$$

Fick's law

flux $\vec{J} = -D\dfrac{\partial c}{\partial r}$

$$\frac{\partial c}{\partial t} = -\vec{\nabla}\cdot\vec{J} = D\frac{\partial^2 c}{\partial r^2}$$

$$D_0 = k_D M^{-b} = \frac{k_B T}{6\pi\eta R_h}$$

$$b \approx \frac{1+a}{3}$$

$$[\eta] = K_{MH} M^a$$

hydrodynamics radius: R_h

Effective viscosity of suspensions

For the solution of impenetrable spheres of radius ***R***, Einstein derived the Effective viscosity of suspensions

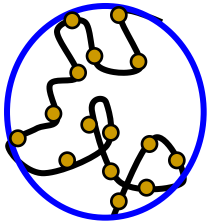
$$\eta = \eta_0 \left(1 + 2.5\Phi\right)$$

η_0: viscosity of pure solvent

Φ: volume fraction occupied by the suspensions in the solution.

If each sphere consists of ***n*** particles (monomer units) of mass ***m***, and their density is c , we have

$$\Phi = N\frac{4}{3}\pi R^3 / V = \frac{N_A c}{M}\frac{4}{3}\pi R^3$$



$nm=M$

Instrinsic viscosity (特性粘数)

$$[\eta] = \left[\frac{\eta - \eta_0}{\eta_0 c}\right]_{c\to 0}$$

N_A : Avogadro Number

$$[\eta] = \frac{2.5\Phi}{c} = 2.5 N_A \frac{4\pi R^3/3}{M} = 2.5 N_A \frac{V_h}{M}$$

V_h hydrodynamics volume

$[\eta]$ dependence of MW: Flory-Fox equation

$$[\eta]=\phi\frac{\left\langle h^2\right\rangle^{3/2}}{M}=\phi\left[\frac{\left\langle h^2\right\rangle}{M}\right]^{3/2}M^{1/2}$$

ϕ_0 is calculated by Rouse-Zimm Theory and confirmed by experiments

$$\alpha=\left(h^2/h_0^2\right)^{1/2}\sim N^{\nu-0.5}$$

扩张因子

$$[\eta]=\phi\left[\frac{\left\langle h_0^2\right\rangle}{M}\right]^{3/2}M^{1/2}\alpha^3$$

$$[\eta]_\Theta=\phi_0\left[\frac{\left\langle h_0^2\right\rangle}{M}\right]^{3/2}M^{1/2}$$

χ=1/2

$$\phi_0=2.84\times10^{23}mol^{-1}$$

For Θ solution

$\left\langle h_0^2\right\rangle\sim M^1$ $[\eta]\sim M^{0.5}$

For flexible chain in good solvent

$\left\langle h^2\right\rangle\sim M^{6/5}$ $[\eta]\sim M^{0.8}$

For stiff chain

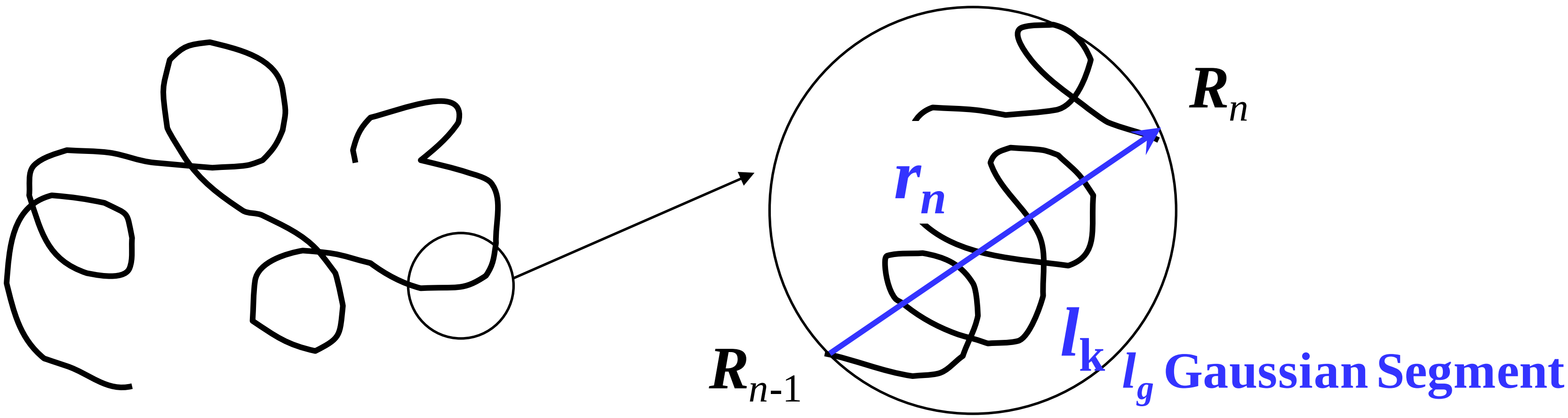
$\left\langle h^2\right\rangle\sim M^2$ $[\eta]\sim M^2$

Mark-Houwink Relation $[\eta]=KM^a$

For flexible chain $\boxed{a=0.5\sim0.8}$

For stiff chain $\boxed{a=0.8\sim1.2}$

A Brief Review of Gaussian Model



小高斯链段的末端距分布 $$\psi = \left(\frac{3}{2\pi l_k^{\ 2}}\right)^{3/2} \exp\left(-\frac{3\boldsymbol{r}_n^{\ 2}}{2l_k^{\ 2}}\right) = A\exp\left(-\frac{u_0(\boldsymbol{r}_n)}{k_B T}\right)$$

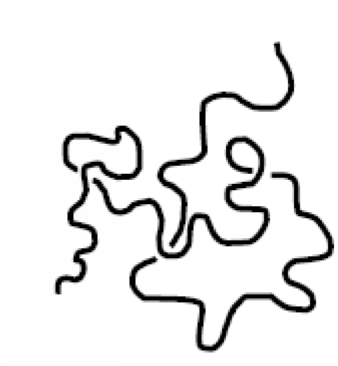
$$u_0(\boldsymbol{r}_n) = \frac{3}{2l_k^2} k_B T (\boldsymbol{R}_n - \boldsymbol{R}_{n-1})^2$$ 熵弹簧

高斯长链 $$\Phi(\boldsymbol{R}) = \prod_{n=1}^{n_g} \psi = \left(\frac{3}{2\pi l_g^2}\right)^{3n_g/2} \exp\left(-\frac{1}{k_B T}\sum_{n=1}^{n_g} u_0(\boldsymbol{r}_n)\right)$$

$$= \left(\frac{3}{2\pi l_g^2}\right)^{3n_g/2} \exp\left(-\frac{U_0(\{\boldsymbol{r}_{n_g}\})}{k_B T}\right)$$

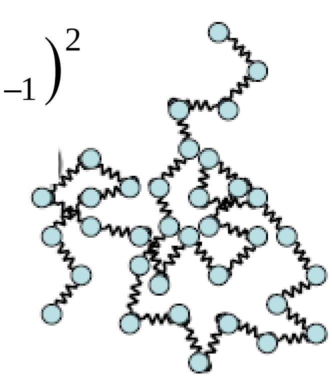
$$U_0(\{\boldsymbol{r}_{n_g}\}) = \frac{3}{2l_g^2} k_B T \sum_{n=1}^{n_g} (\boldsymbol{R}_n - \boldsymbol{R}_{n-1})^2$$

Rouse-Zimm Model



$$U = \frac{k}{2}\sum_{n=2}^{N}\left(\boldsymbol{R}_n - \boldsymbol{R}_{n-1}\right)^2$$

$$k = \frac{3k_BT}{b^2}$$



Spring force

$$F_n^s = -\frac{\partial U}{\partial \boldsymbol{R}_n} = k\frac{\partial^2 \boldsymbol{R}_n}{\partial n^2}$$

Local drag

$$F_n^d = -\zeta \boldsymbol{v}_n = -\zeta\frac{\partial \boldsymbol{R}_n}{\partial t}$$

Random force of Brownian Motion

$$\left\langle \boldsymbol{f}_\alpha\left(n,t\right)\boldsymbol{f}_\beta\left(m,t'\right)\right\rangle = 2\zeta k_BT\delta_{\alpha\beta}\delta\left(n-m\right)\delta\left(t-t'\right)$$

$$\left\langle \boldsymbol{f}\left(n,t\right)\right\rangle = 0$$

$$\boxed{k\frac{\partial^2 \boldsymbol{R}_n}{\partial n^2} - \zeta\frac{\partial \boldsymbol{R}_n}{\partial t} + \boldsymbol{f}\left(n,t\right) = 0}$$

Rouse-Zimm Model

$$R_H = \frac{1}{8}\sqrt{\frac{3\pi}{2}}\sqrt{N}b = 0.66467 R_g$$

$$D_G = \frac{k_B T}{\zeta_0} = \frac{k_B T}{6\pi\eta R_H} = 0.196\frac{k_B T}{6\pi\eta\sqrt{N}b}$$

$$[\eta] = 0.425\frac{N_A}{M}\left(\sqrt{N}a\right)^3 = \frac{\phi}{M}\left(\sqrt{6}R_g\right)^3$$

$$\phi_{0(\mathrm{RZ})} = 0.425 N_A = 2.56\times 10^{23}$$

$$\phi_{0(\exp)} = 2.2 \sim 2.87\times 10^{23}$$