Chapter 3 Polymer Solutions

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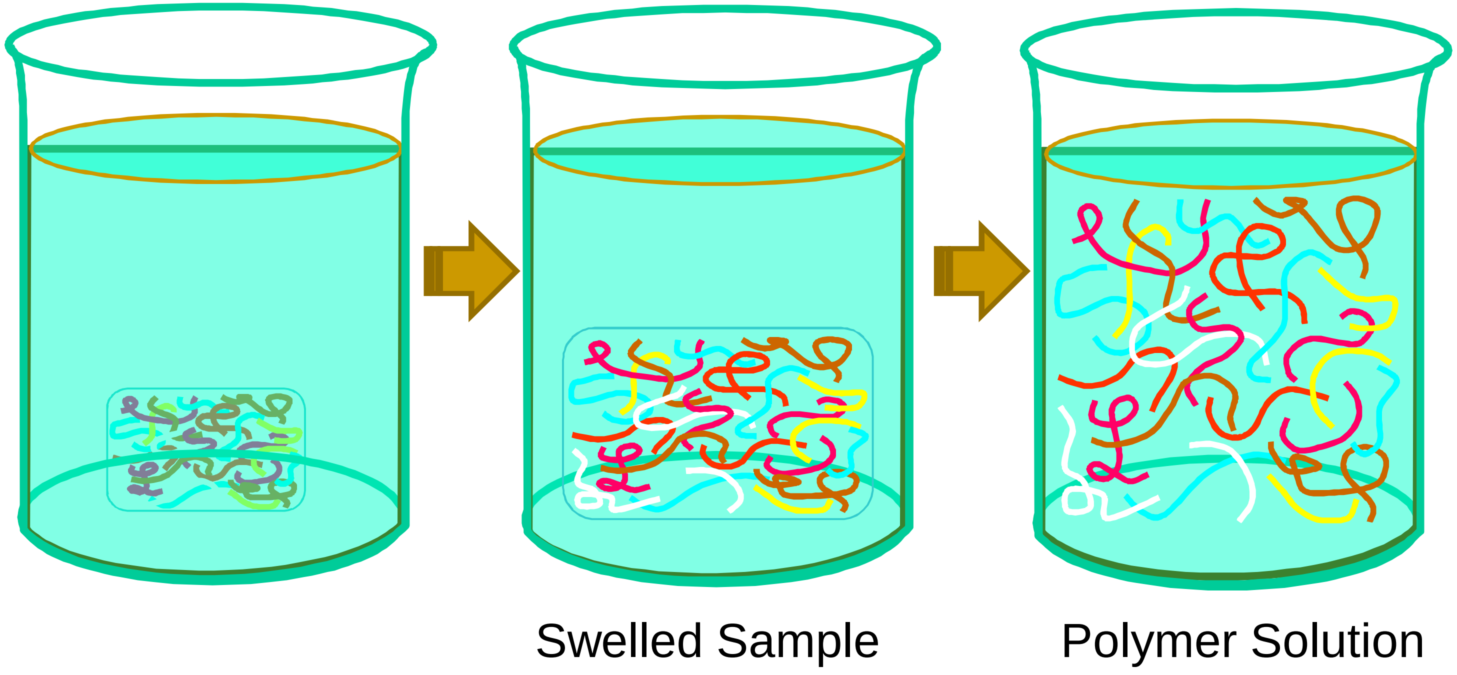
Chapt. 3 Polymer Solutions

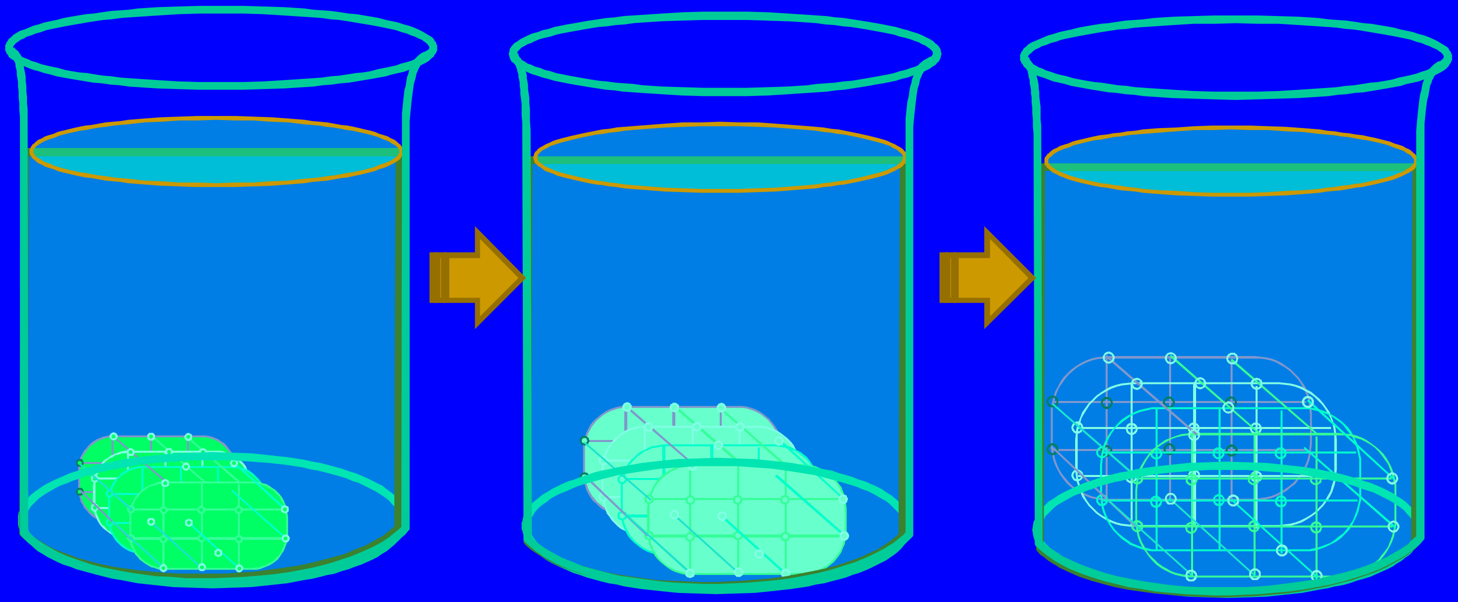
- **The solution process (linear Polymer)**



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

先溶胀，后溶解

Crosslinked polymers: only can be swelled



有溶胀，无溶解

Crystalline polymers

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.

先熔融，后溶解

3.1 Interactions in Polymer System

van der Waals interactions

1. electrostatic interaction

Keesom force $E_K = -\frac{2}{3}\frac{\mu_1^2\mu_2^2}{r^6 k_B T}$ between permanent charges

2. Induction (polarization) interaction

Debye force $E_D = \frac{-(\alpha_1\mu_2^2 + \alpha_2\mu_1^2)}{r^6}$ between a permanent multipole on one molecule with an induced multipole on another

3. Dispersion interaction

London force $E_L = -\frac{3}{2}\left(\frac{I_1 I_2}{I_1 + I_2}\right)\left(\frac{\alpha_1\alpha_2}{r^6}\right)$ between any pair of molecules, including non-polar atoms, arising from the interactions of instantaneous multipoles.

μ: Dipole moment α: Polarizability $\alpha_\mu = \frac{\mu^2}{3k_B T}$ I: Ionization energy

- Long-range Coulomb interactions

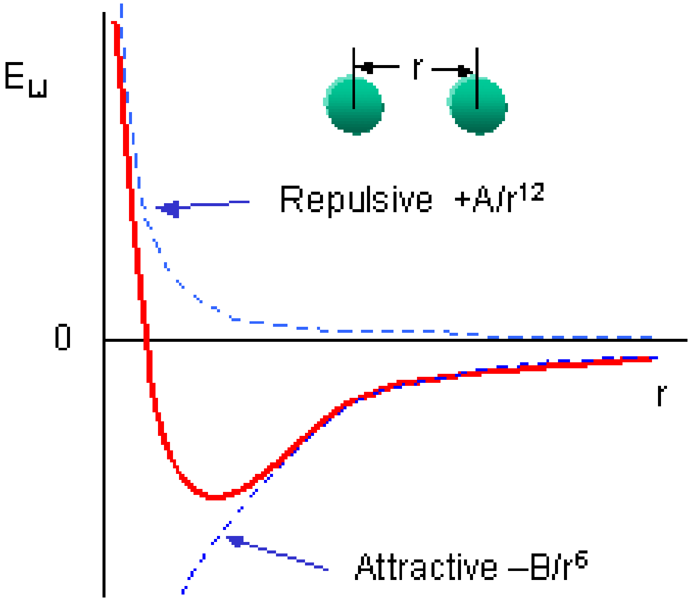
see 3.8

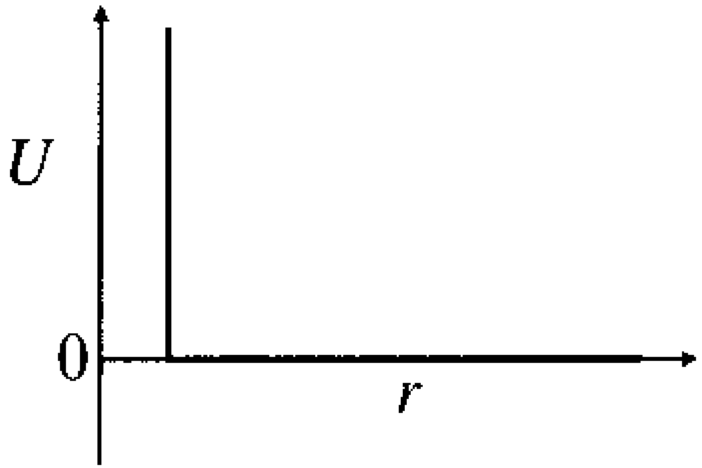
$$U(r) = \frac{Q_1 Q_2 e^2}{4\pi\varepsilon_0 k_B T r}$$

- Hydrogen bond interactions

The Lennard-Jones or Hard Core Potential

- The L-J (6-12) Potential is often used as an approximate model for a total (repulsion plus attraction) van der Waals force as a function of distance.





$$U_{LJ} = \frac{A}{r^{12}} - \frac{B}{r^{6}}$$

$$U = 0 \quad r > r_0$$

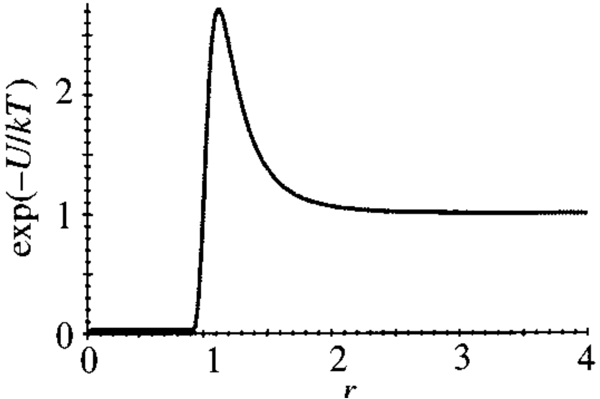
$$U = \infty \quad r \leq r_0$$

Mayer *f*-Function and Excluded Volume

The Probability *P*(*r*) of finding two monomers at distance *r*:

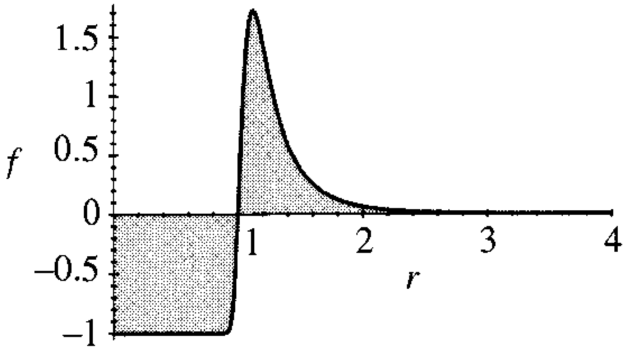
Boltzmann factor

$P(r) \propto \exp[-U(r)/(k_B T)]$



Mayer *f*-function: difference of Boltzmann factor for two monomers at *r* and at ∞

$f(r) = \exp(-U(r)/k_B T) - 1$



Exclude Volume *v*:

$$v = -\int f(r)\, d^3r = \int (1 - \exp[-U(r)/(k_B T)])d^3r$$

3.2 Criteria (判据) of Polymer Solubility

- **Gibbs free energy of mixing**

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

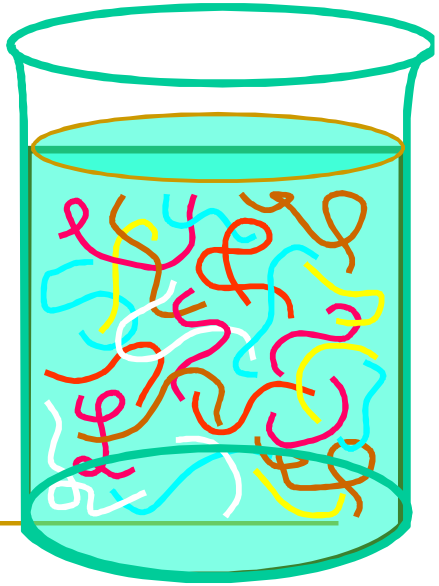
$$\Delta S_{mix} > 0$$

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

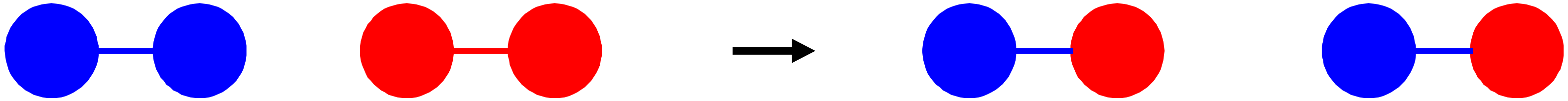
Entropy of mixing for ideal solution

$$\Delta S^{i}_{mix} = -k\left(N_1 \ln X_1 + N_2 \ln X_2\right) > 0$$

$$\Delta H_{mix} \ ???$$



1. Hildebrand enthalpy of mixing (混合焓)



1-1 + 2-2 ⟶ 1-2 + 1-2

1: solvent; 2: polymer

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

($\Delta E/v$) cohesive energy density

(摩尔内聚能密度)

P_{12} total pairs of [1-2]

$$\Delta H_{mix} = \left(\left(\frac{\Delta E_1}{v_1} \right)^{1/2} - \left(\frac{\Delta E_2}{v_2} \right)^{1/2} \right)^2 n_2 \bar{V}_2 \, \phi_1 \left(\frac{V_m}{V_m} \right)$$

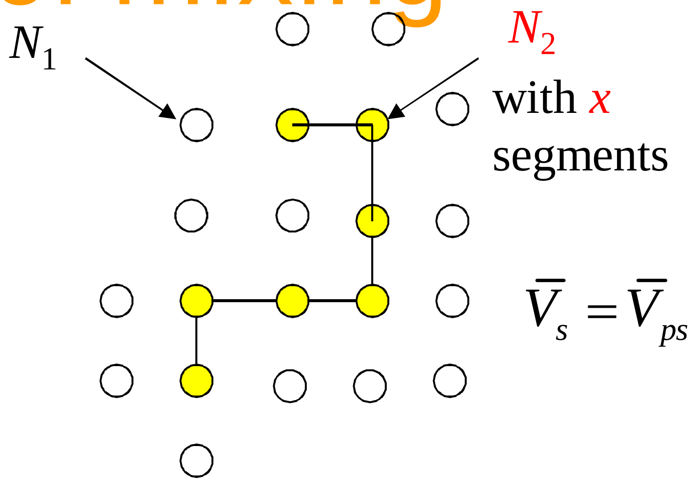
$$\frac{n_2 \bar{V}_2}{V_m} = \phi_2 \qquad \frac{n_1 \bar{V}_1}{V_m} = \phi_1$$

$$= \left(\left(\frac{\Delta E_1}{v_1} \right)^{1/2} - \left(\frac{\Delta E_2}{v_2} \right)^{1/2} \right)^2 n_1 \bar{V}_1 \, \phi_2 \left(\frac{V_m}{V_m} \right) = V_m \phi_1 \phi_2 \left(\left(\frac{\Delta E_1}{v_1} \right)^{1/2} - \left(\frac{\Delta E_2}{v_2} \right)^{1/2} \right)^2$$

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

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

2. Huggin’s Enthalpy of mixing

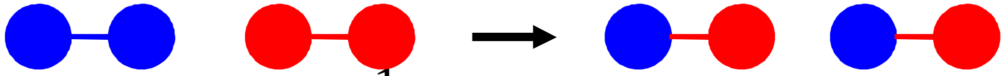


$$\bar{V}_s = \bar{V}_{ps}$$

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



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

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

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

cells surrounding a polymer

number of polymers

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

$$\phi_1 = \frac{N_1}{N_1+xN_2} = \frac{\bar{V}_s N_1}{V_m} \text{ and } \phi_2 = \frac{xN_2}{N_1+xN_2} = \frac{xN_2\bar{V}_s}{V_m}$$

$$\Delta H_{mixing} = (Z-2)N_1\phi_2\Delta\varepsilon_{12} = (Z-2)xN_2\phi_1\Delta\varepsilon_{12}$$

$$\Delta H_{mixing} = kT\chi N_1\phi_2 = RT\chi n_1\phi_2 = \frac{V_m}{\bar{V}_s}kT\chi\phi_1\phi_2 = V_m\phi_1\phi_2[\delta_1-\delta_2]^2/\tilde{N}$$

$$\boxed{\chi = \frac{(Z-2)\Delta\varepsilon_{12}}{kT}} = \frac{\bar{V}_s(\delta_1-\delta_2)^2}{RT}$$

Flory-Huggins parameter: (interaction parameter)

另类导法

$$H_{11}=\frac{1}{\bar{V}_s}\int\varepsilon_{11}\phi_1^2\left(r\right)dr=\frac{\varepsilon_{11}}{\bar{V}_s}\int\phi_1\left(r\right)\left(1-\phi_2\left(r\right)\right)dr$$

$$=\frac{\varepsilon_{11}}{\bar{V}_s}\int\phi_1\left(r\right)dr-\frac{\varepsilon_{11}}{\bar{V}_s}\int\phi_1\left(r\right)\phi_2\left(r\right)dr=\frac{V_m}{\bar{V}_s}\left(\varepsilon_{11}\phi_1-\varepsilon_{11}\phi_1\phi_2\right)$$

$$H_{22}=\varepsilon_{22}\phi_2^2\frac{V_m}{\bar{V}_s}=\varepsilon_{22}\phi_2\left(1-\phi_1\right)\frac{V_m}{\bar{V}_s}=\frac{V_m}{\bar{V}_s}\left(\varepsilon_{22}\phi_2-\varepsilon_{22}\phi_1\phi_2\right)$$

$$H_{12}=\frac{V_m}{\bar{V}_s}\varepsilon_{12}\phi_1\phi_2$$

$$\Delta H_{mixing}=H_{12}-\frac{1}{2}\left(H_{11}+H_{22}\right)=\frac{V_m}{\bar{V}_s}\left(\varepsilon_{12}-\frac{1}{2}\left(\varepsilon_{11}+\varepsilon_{22}\right)\right)\phi_1\phi_2+const.$$

$$\boxed{=\frac{V_m}{\bar{V}_s}\chi\phi_1\phi_2}+const.$$

另类导法

$$H_{11} = \frac{1}{2\bar{V}_s}\int \varepsilon_{11}\phi_1^2(r)dr = \frac{\varepsilon_{11}}{2\bar{V}_s}\int \phi_1(r)\big(1-\phi_2(r)\big)dr$$

$$= \frac{\varepsilon_{11}}{2\bar{V}_s}\int \phi_1(r)dr - \frac{\varepsilon_{11}}{2\bar{V}_s}\int \phi_1(r)\phi_2(r)dr = \frac{V_m}{2\bar{V}_s}\left(\varepsilon_{11}\phi_1 - \varepsilon_{11}\phi_1\phi_2\right)$$

$$H_{22} = \varepsilon_{22}\phi_2^2\frac{V_m}{2\bar{V}_s} = \varepsilon_{22}\phi_2(1-\phi_1)\frac{V_m}{2\bar{V}_s} = \frac{V_m}{2\bar{V}_s}\left(\varepsilon_{22}\phi_2 - \varepsilon_{22}\phi_1\phi_2\right)$$

$$H_{12} = \frac{V_m}{\bar{V}_s}\varepsilon_{12}\phi_1\phi_2$$

$$\phi_1 = \frac{\bar{V}_s N_1}{V_m} \qquad H_{11}^0 = \varepsilon_{11}\frac{V_s^0}{2\bar{V}_s} = \varepsilon_{11}\frac{N_1}{2}$$

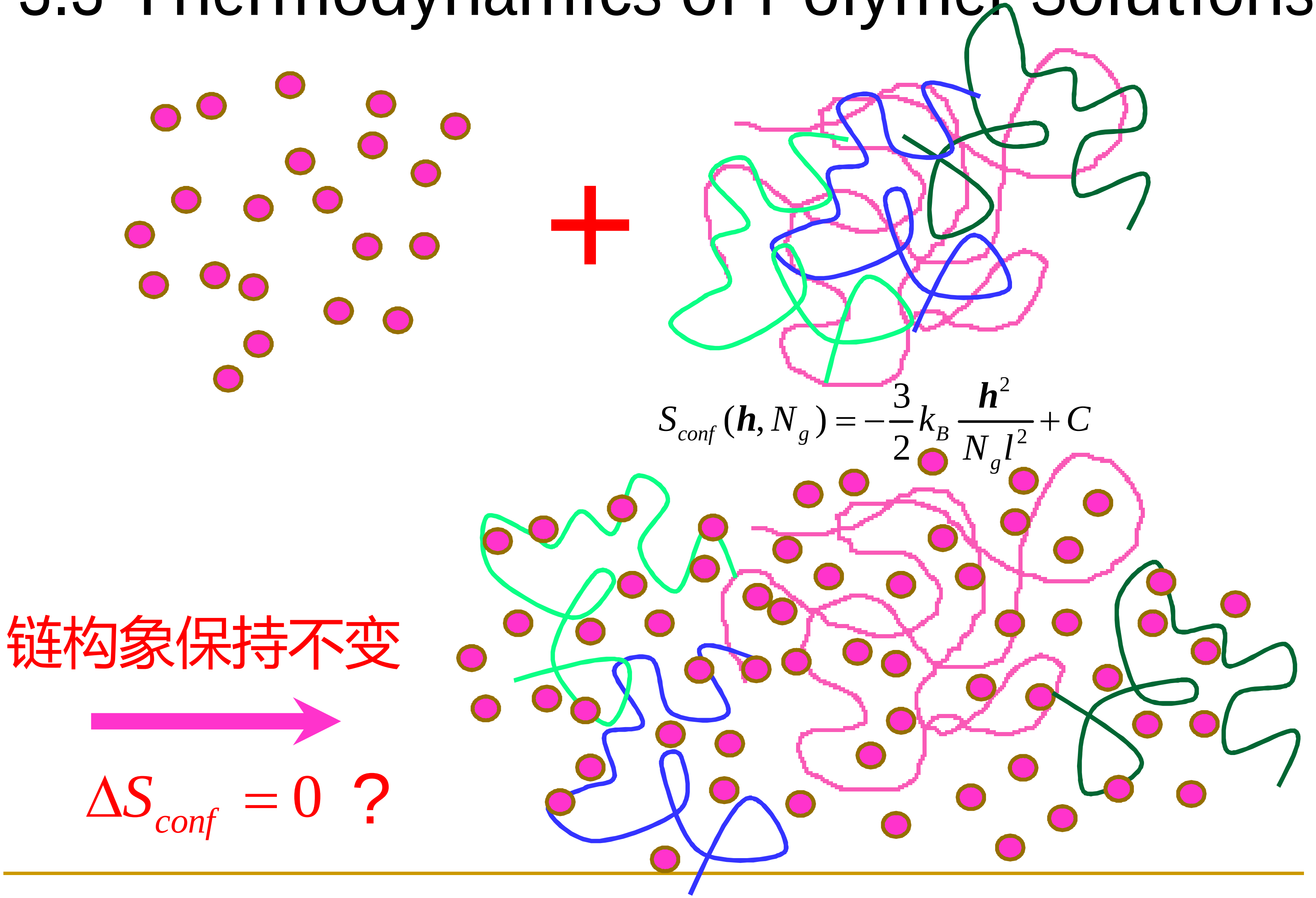
$$\phi_2 = \frac{xN_2\bar{V}_s}{V_m} \qquad H_{22}^0 = \varepsilon_{22}\frac{V_p^0}{2\bar{V}_s} = \varepsilon_{22}\frac{xN_2}{2}$$

$$\Delta H_{mixing} = H_{12} + \left(H_{11} + H_{22}\right) - \left(H_{11}^0 + H_{22}^0\right)$$

$$= \frac{V_m}{\bar{V}_s}\left(\varepsilon_{12} - \frac{1}{2}\left(\varepsilon_{11} + \varepsilon_{22}\right)\right)\phi_1\phi_2 = \boxed{\frac{V_m}{\bar{V}_s}kT\chi\phi_1\phi_2}$$

$$V_s^0 + V_p^0 = V_m$$

3.3 Thermodynamics of Polymer Solutions



$$S_{conf}(\boldsymbol{h}, N_g) = -\frac{3}{2}k_B\frac{\boldsymbol{h}^2}{N_g l^2} + C$$

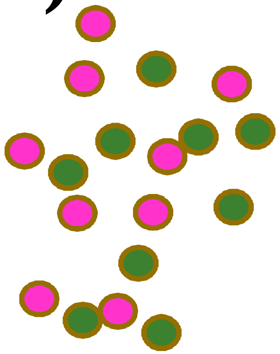
链构象保持不变

$\Delta S_{conf} = 0$ ？

与溶剂混合会产生各种排列组合状态, 即混合熵$\Delta S_m > 0$

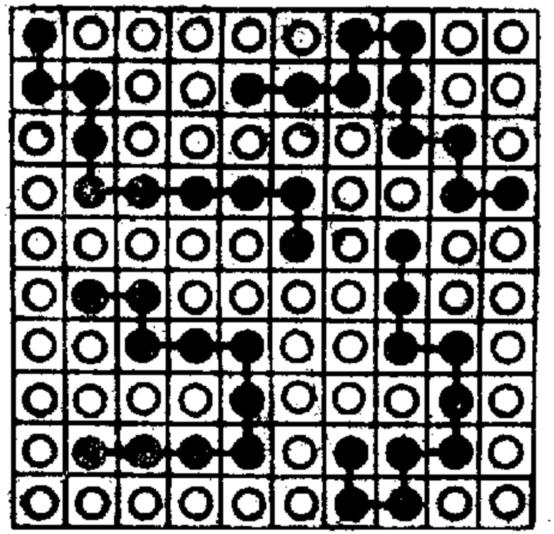
3.3 Thermodynamics of Polymer Solutions

(1) Entropy of mixing for ideal solution



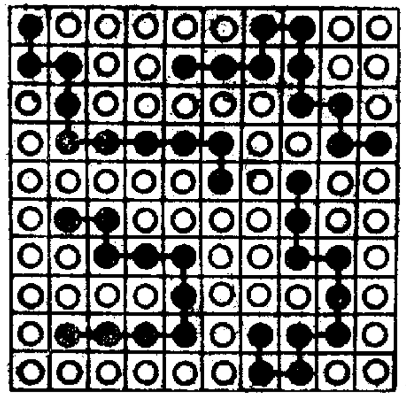
$$\Delta S_{mix}^{i} = -k\left(N_1 \ln X_1 + N_2 \ln X_2\right)$$

(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.

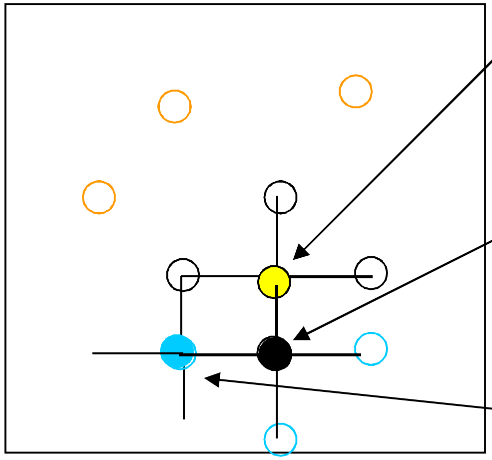
Flory-Huggins theory (Lattice Model (格子模型))



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: $N=N_1+xN_2$ $\phi_1=\frac{N_1}{N_1+xN_2}$ $\phi_2=\frac{xN_2}{N_1+xN_2}$

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

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

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

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

总方式

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

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

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$x$! ≈ $x$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,

$$\Delta S_{mixing} = S_{solution} - (S_{solvent} + S_{polymer}) \qquad \Delta S_{conf} = 0$$

$$= -k\left[N_1 \ln\frac{N_1}{N_1 + xN_2} + N_2 \ln\frac{xN_2}{N_1 + xN_2} \right]$$

where $\phi_1 = \frac{N_1}{N_1 + xN_2} = \frac{n_1}{n_1 + xn_2} = \frac{N_1\bar{V}_s}{V_m} = \frac{\tilde{N}n_1\bar{V}_s}{V_m}$ $\qquad \phi_2 = \frac{xN_2}{N_1 + xN_2} = \frac{xn_2}{n_1 + xn_2} = \frac{xN_2\bar{V}_s}{V_m} = \frac{\tilde{N}xn_2\bar{V}_s}{V_m}$

$$\Delta S_{mixing} = -k\left[N_1 \ln\phi_1 + N_2 \ln\phi_2\right] \quad = -R\left[n_1 \ln\phi_1 + n_2 \ln\phi_2\right]$$

$$= -k\frac{V_m}{\bar{V}_s}\left[\phi_1 \ln\phi_1 + \frac{\phi_2}{x}\ln\phi_2\right]$$

Free Energy of FH Theory

Huggins Enthalpy: $\Delta H_{mixing} = kT\chi N_1\phi_2 = RT\chi n_1\phi_2 = \frac{V_m}{\bar{V}_s}kT\chi\phi_1\phi_2$

$$\phi_1 = \frac{x_1N_1}{x_1N_1 + x_2N_2} = \frac{x_1n_1}{x_1n_1 + x_2n_2} = \frac{x_1N_1\bar{V}_s}{V_m} = \frac{\tilde{N}x_1n_1\bar{V}_s}{V_m} \quad \phi_2 = \frac{x_2N_2}{x_1N_1 + x_2N_2} = \frac{x_2n_2}{x_1n_1 + x_2n_2} = \frac{x_2N_2\bar{V}_s}{V_m} = \frac{\tilde{N}x_2n_2\bar{V}_s}{V_m}$$

Gibbs Free Energy $\Delta G_{mixing} = \Delta H_{mixing} - T\Delta S_{mixing}$

$$\Delta G_{mixing} = kT\left(N_1\ln\phi_1 + N_2\ln\phi_2 + \chi x_1N_1\phi_2\right)$$

分子数

$$= RT\left(n_1\ln\phi_1 + n_2\ln\phi_2 + \chi x_1n_1\phi_2\right)$$

摩尔数

$$= \boxed{kT\frac{V_m}{\bar{V}_s}}\left(\frac{\phi_1}{x_1}\ln\phi_1 + \frac{\phi_2}{x_2}\ln\phi_2 + \chi\phi_1\phi_2\right)$$

通式

$$\Delta F_m = \frac{\bar{V}_s}{V_m}\frac{\Delta G_m}{kT} = \left(\frac{\phi_1}{x_1}\ln\phi_1 + \frac{\phi_2}{x_2}\ln\phi_2 + \chi\phi_1\phi_2\right)$$

For Polymer Solutions $x_1=1$

Chemical potentials (化学位):

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

(for solvent)

$$= \frac{\bar{V}_s}{V_m}\left(\Delta G_m - \phi_2\frac{\partial\Delta G_m}{\partial\phi_2}\right) = RT\left(\Delta F_m - \phi_2\frac{\partial\Delta F_m}{\partial\phi_2}\right)$$

$$\Delta F_m = \frac{\bar{V}_s}{V_m}\frac{\Delta G_m}{kT}$$

$$= \left(\phi_1\ln\phi_1 + \frac{\phi_2}{x}\ln\phi_2 + \chi\phi_1\phi_2\right)$$

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

(for polymer)

$$= \frac{\bar{V}_s}{V_m}\left(\Delta G_m - \phi_1\frac{\partial\Delta G_m}{\partial\phi_1}\right) = RT\left(\Delta F_m - \phi_1\frac{\partial\Delta F_m}{\partial\phi_1}\right)$$

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

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

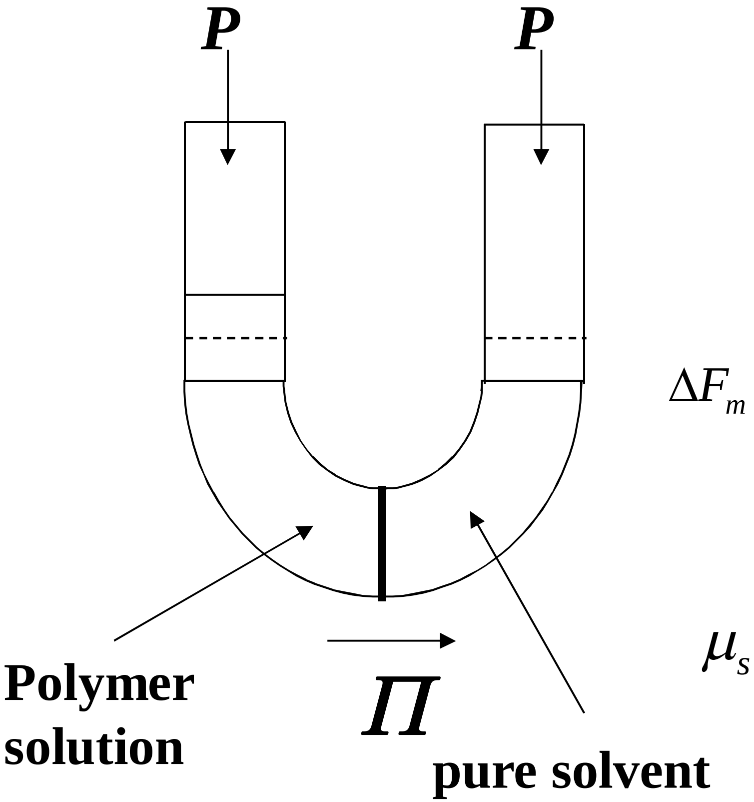
χ=1/2, **有热效应的“理想溶液”???**

χ < 1/2, good solvent
χ = 1/2, theta Θ solvent
χ > 1/2, poor solvent

Osmotic pressure (滲透压):

$$\mu_s(\phi_2, P+\Pi, T) = \mu_s(0, P, T)$$

$$G(n_p, n_s, P, T) = G_m + PV_m = G_m + P(n_p x + n_s)\bar{V}_s$$



$$\mu_s(\phi_2, P, T) = \frac{\partial}{\partial n_s}\left[G(n_p, n_s, P, T)\right]_{T,P,n_p}$$

$$= \mu_s^0 + \left[\frac{\partial(\Delta G_m)}{\partial n_s}\right]_{T,P,n_p} + P\bar{V}_s$$

$$\Delta F_m = \frac{\bar{V}_s}{V_m}\frac{\Delta G_m}{kT}$$

$$\left[\frac{\partial(\Delta G_m)}{\partial n_s}\right]_{T,P,n_p} = RT\left(\Delta F_m - \phi_2\frac{\partial \Delta F_m}{\partial \phi_2}\right)$$

$$\mu_s(\phi_2, P, T) = \mu_s^0 + RT\left(\Delta F_m - \phi_2\frac{\partial \Delta F_m}{\partial \phi_2}\right) + P\bar{V}_s$$

$$\because \mu_s(\phi_2, P+\Pi, T) = \mu_s(0, P, T)$$

$$V_m = (n_p x + n_s)\bar{V}_s$$

$$\boxed{\therefore \Pi = \frac{RT}{\bar{V}_s}\left(\phi_2\frac{\partial \Delta F_m}{\partial \phi_2} - \Delta F_m\right)}$$

Osmotic pressure (渗透压):

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

$$\Delta F_m = \frac{\bar{V}_s}{V_m}\frac{\Delta G_m}{kT} = \left(\phi_1 \ln\phi_1 + \frac{\phi_2}{x}\ln\phi_2 + \chi\phi_1\phi_2\right)$$

$$A_{2\phi} = \frac{\left(\frac{1}{2} - \chi\right)}{\bar{V}_s}$$

second Virial coefficent

$$\boxed{\phi = \frac{c}{\rho_2}, \quad \rho_2 = \frac{M}{x\bar{V}_s}}$$

$$\Pi = RT\left[\frac{c}{M} + A_2 c^2\right] \qquad A_{2c} = \frac{\left(\frac{1}{2} - \chi\right)}{\bar{V}_1\rho_2^2}$$

当ϕ_2<<1/x(0.5-χ)或χ=1/2

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

当ϕ_2>>1/x, 即ϕ_2^2>> ϕ_2 /x

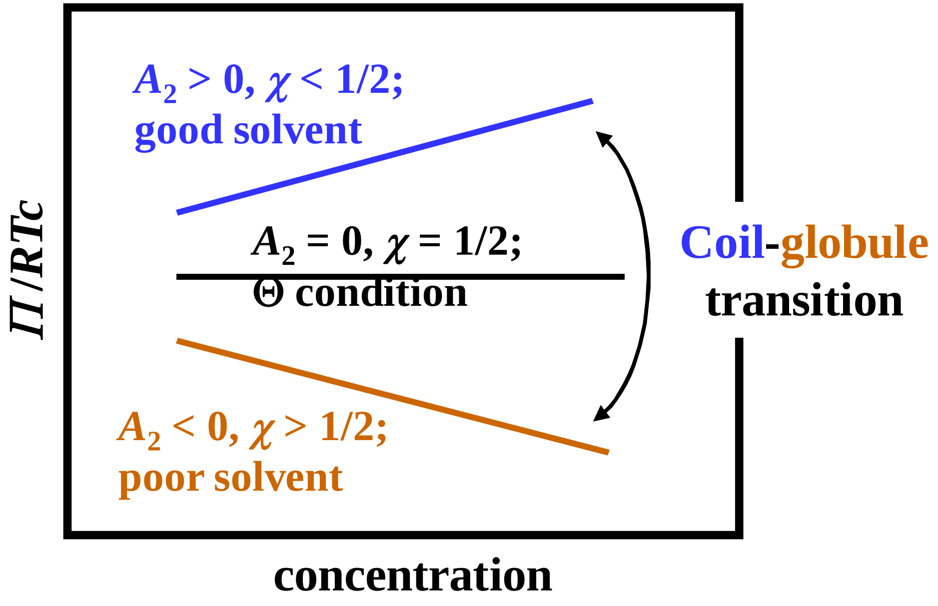
$$\xcancel{\Pi \sim \phi_2^2}$$

???

Polymer Shapes in Dilute Solutions

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

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



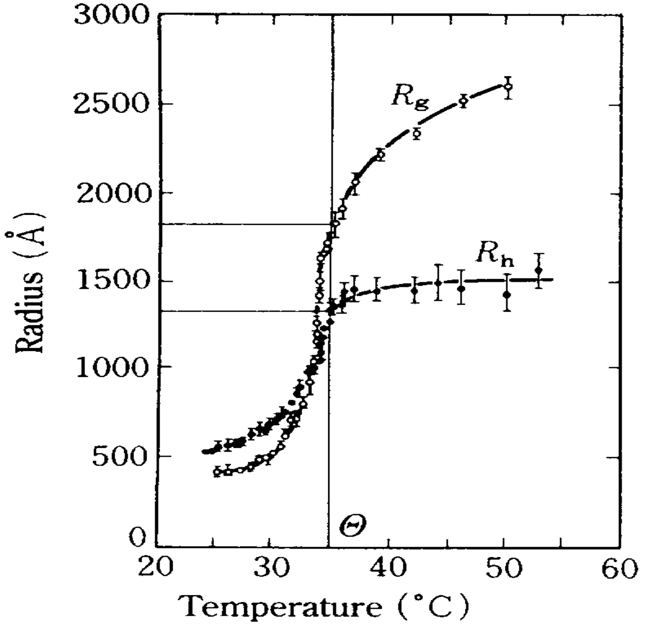
$A_2 > 0, \chi < 1/2$; good solvent

$A_2 = 0, \chi = 1/2$; Θ condition

$A_2 < 0, \chi > 1/2$; poor solvent

Coil-globule transition

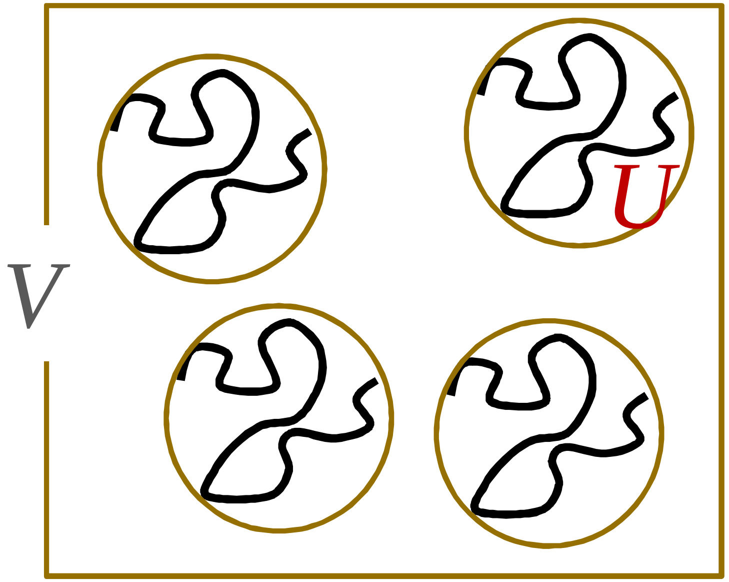
$\chi \sim 1/kT$!!!



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.**)**

3.4 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

$$\Omega \approx (1-U/V)^0(1-U/V)^1\ldots(1-U/V)^{(N_2-1)}$$

$$\approx\left(1-\frac{U}{V}\right)^{N_2(N_2-1)/2}\approx\left(1-\frac{U}{V}\right)^{N_2^2/2}$$

or $\Omega\approx\prod_{i=0}^{N_2-1}\left(1-\frac{iU}{V}\right)$

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

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

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

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

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

A_2

$$U\sim R_g^3\sim T??$$

3.4 Chain Conformations in Dilute Solutions

(2) Flory 稀溶液理论

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

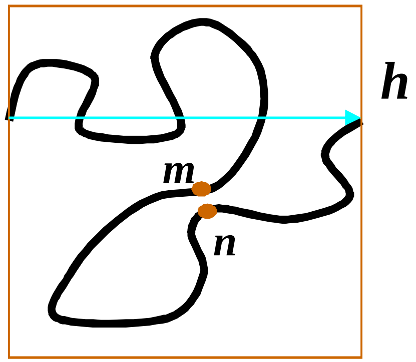
$$W(h,x)=W_0(h,x)\underbrace{\Omega(h)}_{\text{体积排除修正}}\underbrace{\exp\left(-\frac{\bar{E}(h)}{kT}\right)}_{\text{能量权重修正}}$$

体积排除修正：只统计单元间不发生重叠的构象状态，因为一旦发生了重叠，此构象就不能存在。

能量权重修正：每种构象的实现概率还与实现此构象状态的能级有关，能级越高，则实现的概率相应降低；能级越低，则反之。

体积排除修正

(1) $\Omega(h)$



链包含的体积 h^3　链段的体积 $v_c=l^3$

一个链段占有的体积分数v_c/h^3　$\phi_2=\dfrac{xv_c}{h^3}$

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

$$\Omega(h)\approx 1\left(1-\frac{v_c}{h^3}\right)\left(1-2\frac{v_c}{h^3}\right)\ldots=\prod_{i=0}^{x-1}\left(1-i\frac{v_c}{h^3}\right)$$

第一个　第二个　　第三个

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

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

$$\approx\exp\left[-\frac{v_c}{h^3}\sum_{i=0}^{x-1}i\right]=\exp\left[\boxed{-\frac{v_cx^2}{2h^3}}\right]$$

溶液中真实单链构象的径向分布函数$W(h,x)$

(2) $E(h)$

$$\frac{H}{kT}=\frac{V_m}{\bar{V}_s}\chi\phi_1\phi_2 \qquad V_m\approx h^3 \qquad \bar{V}_s=v_c \qquad \phi_2=\frac{xv_c}{h^3}$$

$$\frac{\bar{E}(h)}{kT}=\frac{h^3}{v_c}\chi(1-\phi_2)\phi_2=\frac{h^3}{v_c}\chi\phi_2-\frac{h^3}{v_c}\chi\phi_2^2=x\chi-\frac{h^3}{v_c}\chi\frac{x^2v_c^2}{h^6}$$

$$=const-\chi\frac{x^2v_c}{h^3}$$

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

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

链内两体相互作用能的总和

包括了链段的排斥体积和溶剂-链段相互作用

当χ=1/2, 理想高斯链　　　当χ<1/2, ???

1. Polymer chain in good solvents – method I

$$W(h,x) \propto h^2 \exp\left[-\frac{3h^2}{2xl^2} - \frac{x^2}{2}\frac{v_c}{h^3}(1-2\chi)\right] \qquad \frac{\partial W(h,x)}{\partial h} = 0$$

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

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

$W_0(h,x)$的极值$h_0^*=(2xl^2/3)^{1/2}$

最可几尺寸≈根均方尺寸

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

$$\tau = 1-2\chi$$

$$u = v_c(1-2\chi) = v_c\tau$$

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

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

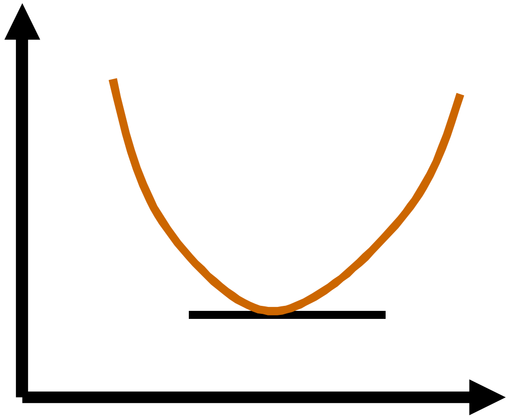
$\chi>1/2$, $\nu=$??

1. Polymer chain in good solvents - method II

单链自由能：$G \sim -k_B T \ln \Phi$ $\quad \Phi(h,x) \propto \exp\left[-\frac{3h^2}{2xl^2} - \frac{x^2}{2}\frac{v_c}{h^3}(1-2\chi)+\dots\right]$

$$G \sim k_B T\left(\frac{3h^2}{2xl^2} + \boxed{\frac{x^2 v_c}{2h^3}(1-2\chi)} + \dots\right)$$

$$\frac{\partial G}{\partial h} = 0$$



$$\boxed{h \propto x^{3/5}(1-2\chi)^{1/5}}$$

$$\phi_2 = \frac{x v_c}{h^3} \qquad \chi<1/2$$

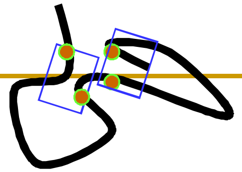
$$G/k_BT \approx \left(\frac{3}{2xl^2h} + \boxed{\frac{\left(\frac{1}{2}-\chi\right)}{v_c}\phi_2^2} + w\phi_2^3\right)h^3$$

second Virial coefficent

conformation entropy + **two body interaction:**

excluded volume repulsion

solvent-segment interaction



Two body interactions are important in good solvents!

Θ Temperature & Θ Solvents

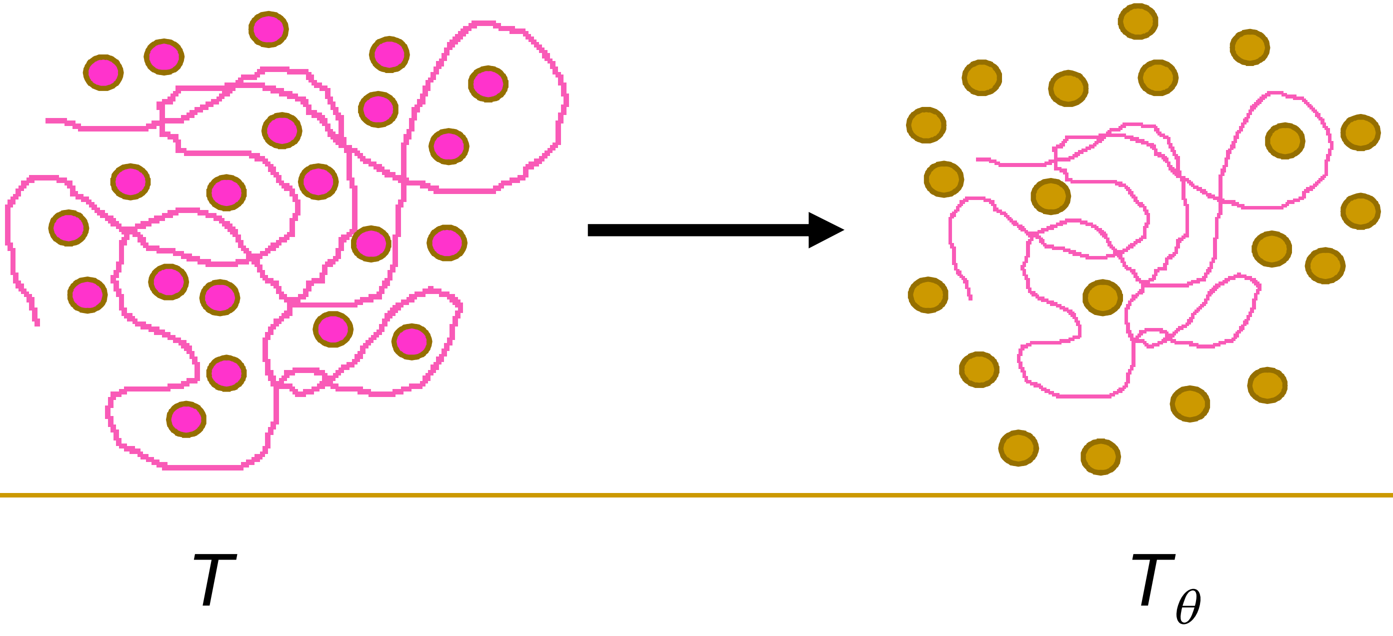
$$\boxed{\chi = 1/2} \longrightarrow \boxed{h^2 \sim N^1}$$

$$\chi_\theta = \frac{(Z-2)\Delta\varepsilon_{12}}{kT_\theta} = \frac{\bar{V}_s\left(\delta_1-\delta_2\right)^2}{RT_\theta} = \frac{1}{2}$$

Θ Solution

$$T_\theta = \frac{2\left(Z-2\right)\Delta\varepsilon_{12}}{k} = \frac{2\bar{V}_s}{R}\left(\delta_1-\delta_2\right)^2$$

Θ Temperature



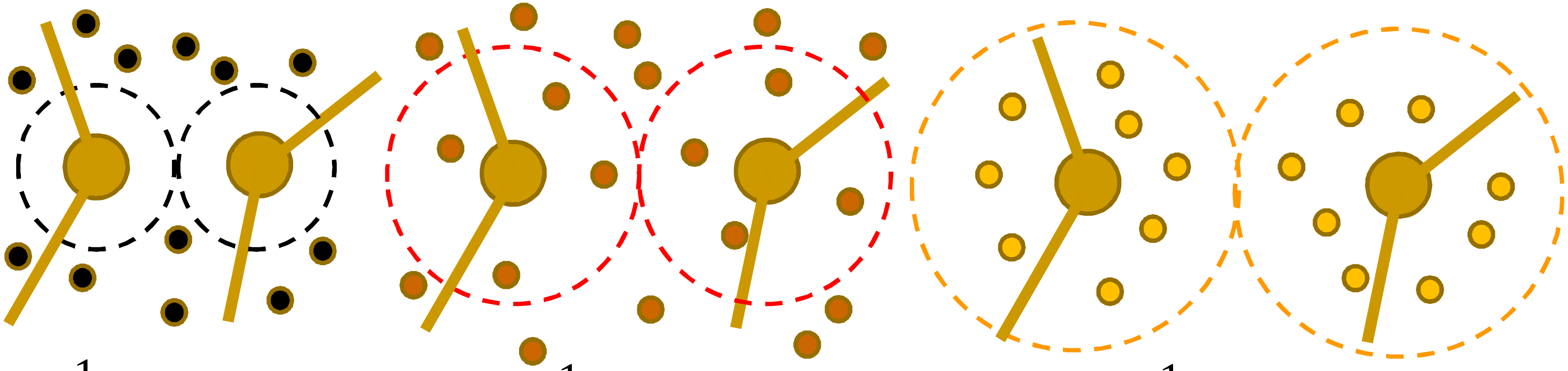
Excluded Volume

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

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

排除体积 $u = v_c(1-2\chi) \approx l_e^3\tau$

$$\boxed{h^* \propto x^\nu (1-2\chi)^{1/5} \propto x^\nu \tau^{1/5}}$$



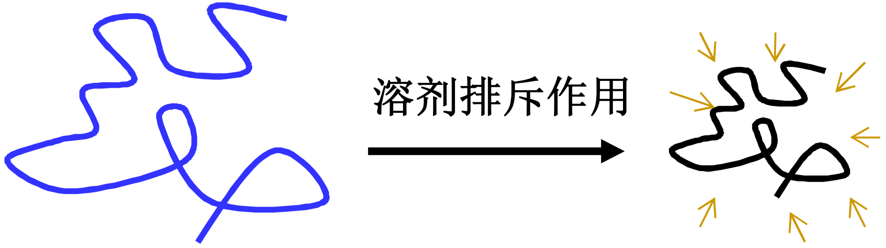
$\chi > \frac{1}{2},\ \langle u\rangle < 0$

$\chi = \frac{1}{2},\ \langle u\rangle = 0$

$\chi < \frac{1}{2},\ \langle u\rangle > 0$

When does the freely jointed chain works

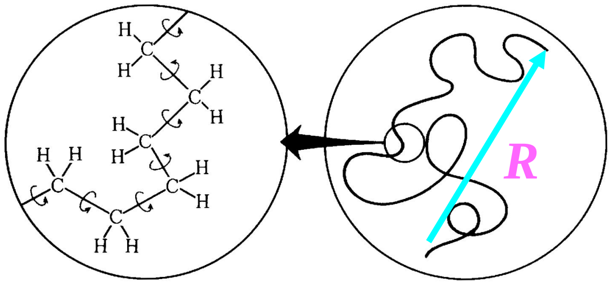
(1) 调节溶剂–链节的作用屏蔽掉体积排除效应和链节–链节相互作用 ⟶ 达到Θ温度的溶液, 测得无扰尺寸$\langle h^2 \rangle_0 \sim N$



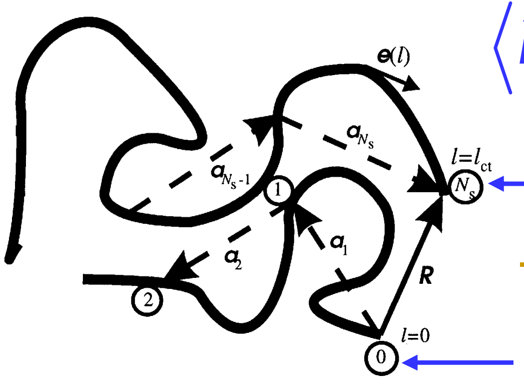
$$\langle h^2 \rangle \sim N^{6/5} \tau^{2/5} \qquad \langle h^2 \rangle_0 \sim N^1$$

(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



“Coarse-grained” (粗粒化) picture:



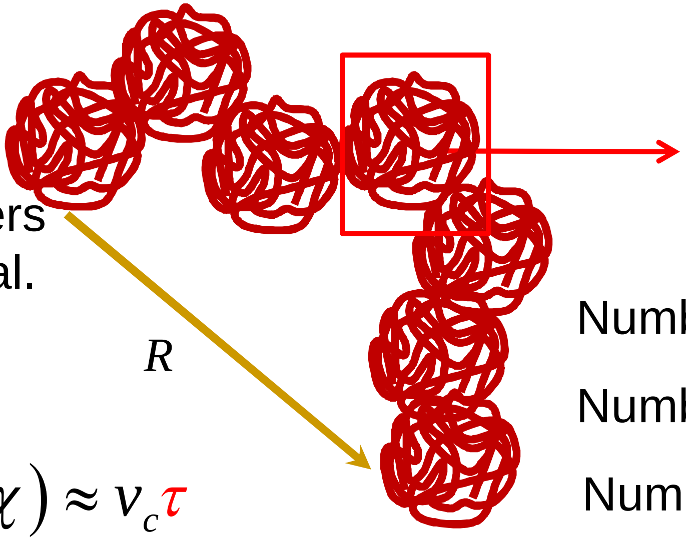
$$\langle h^2 \rangle_0 \sim N_e l_e^2$$

chain end

chain head

Crossover from Gaussian to Swollen

Each polymer chain can be divided into many blobs. Polymers within blobs are ideal.



Thermal Blob $\xi_T = g_T^{1/2} l$

Number of Segments in a Chain: x

Number of Segments in a Blob: g_T

Numbers of Blob in a Chain: x/g_T

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

$$R \propto \xi_T \left(\frac{x}{g_T}\right)^{\frac{3}{5}} = g_T^{1/2}\left(\frac{x}{g_T}\right)^{\frac{3}{5}} l = g_T^{-\frac{1}{10}} x^{\frac{3}{5}} l \quad \boxed{= x^{3/5}\left(\frac{u}{l^3}\right)^{1/5} l}$$

$$g_T = \left(\frac{u}{l^3}\right)^{-2}$$

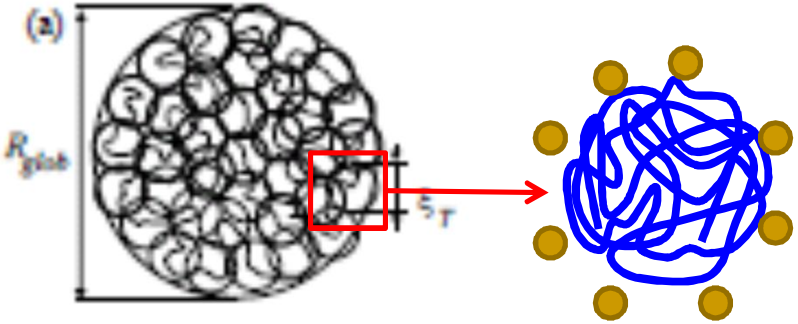
$$\bar{E} \approx k_B T g_T^2 \frac{|u|}{\xi_T^3} \approx k_B T$$

$$\xi_T = \left(\frac{u}{l^3}\right)^{-1} l = \frac{l^4}{u}$$

2. Polymer chain in poor solvents-Method I: **blob model**

Globule:

Blobs:



Blob size: $$\xi_T = g_T^{1/2} l$$

Interaction Energy in a blob: $$\bar{E} \approx k_B T g_T^2 \frac{|u|}{\xi_T^3} \approx k_B T$$

Excluded Volume: $$u \approx l^3 (1-2\chi) \approx l^3 \tau$$

$$g_T = \left(\frac{u}{l^3}\right)^{-2} = |\tau|^{-2} \qquad \xi_T = \left(\frac{u}{l^3}\right)^{-1} l = l|\tau|^{-1}$$

In a Globule: Blobs are densely packed

$$R_{glob}^3 = \xi_T^3 \left(\frac{N}{g_T}\right) \qquad R_{glob}^3 \approx l^3 |\tau|^{-1} N$$

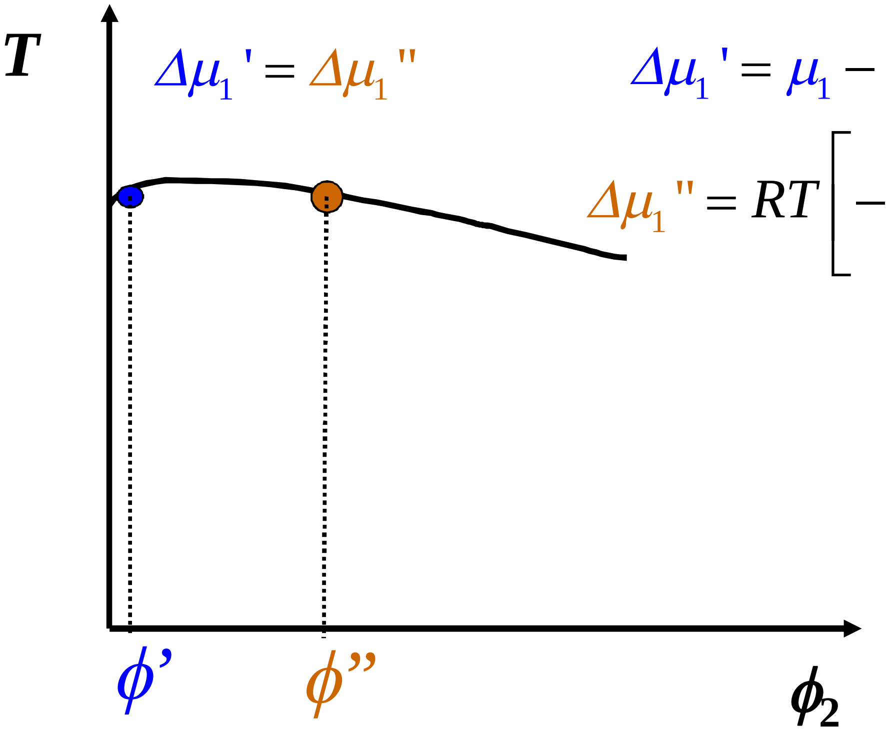
$$\boxed{R_{glob} \approx N^{1/3} l |\tau|^{-1/3}}$$

Interaction Energy in a globule:

$$F_{\text{int}} = -k_B T \frac{N}{g_T} = -k_B T N \tau^2$$

2. Polymer chain in poor solvents-Method II: chemical potential

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



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

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

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

w=1/3

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

In Polymer rich Phase:

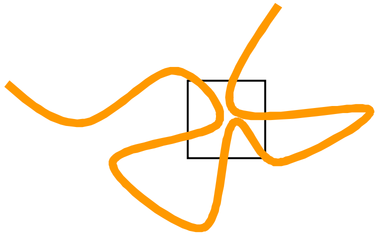
Concentration in Coil: $\phi_{in} = \frac{xv_c}{h^3} \approx \phi_2''$

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

2. Polymer chain in poor solvents-Method III: three body interactions

$\chi > 1/2$

$h \ll h_0$



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

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

$\phi_2 = x v_c / h^3$

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

second Virial coefficent

two body interaction:

excluded volume repulsion

solvent-segment interaction

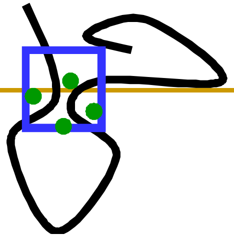
+

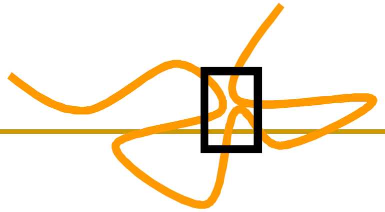
third Virial coefficent

three body repulsion

G=0

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





Three body interactions become important

Flory Formula in Dilute Solutions

$$G \approx k_B T \left(\frac{R^2}{Nl^2} + u \frac{N^2}{R^3} + w \frac{N^3}{R^6} \right)$$

$$R \approx h$$

$$u = v_c (1 - 2\chi)$$

N: Number of Segments in a chain

l: Length of the Kuhn Segment

In good solvents

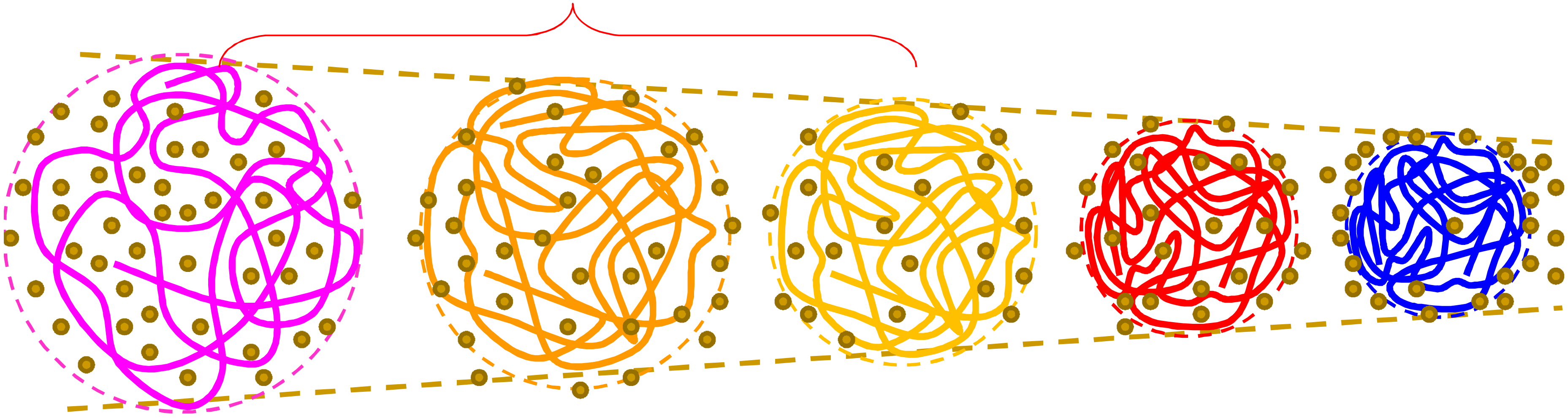
$$G \approx k_B T \left(\frac{R^2}{Nl^2} + u \frac{N^2}{R^3} \right)$$

In poor solvents

$$G \approx k_B T \left(u \frac{N^2}{R^3} + w \frac{N^3}{R^6} \right)$$

Polymer Shapes in Dilute Solutions

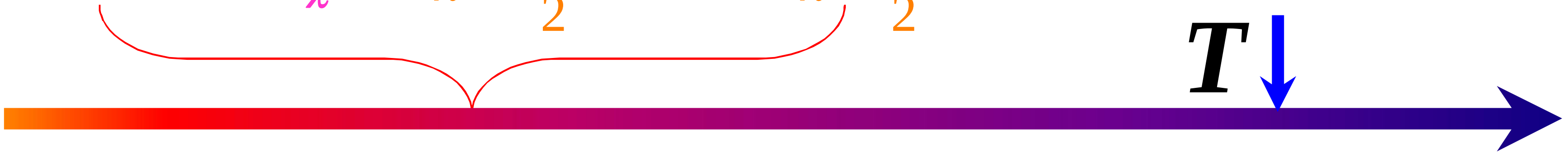
Coil-globule transition



swelling chain **unperturbed chain** **collapsed coil**

$<h>$ $\sim N^{3/5}\tau^{1/5}$ $\sim N^{1/2}$ $\sim N^{1/3}|\tau|^{-1/3}$

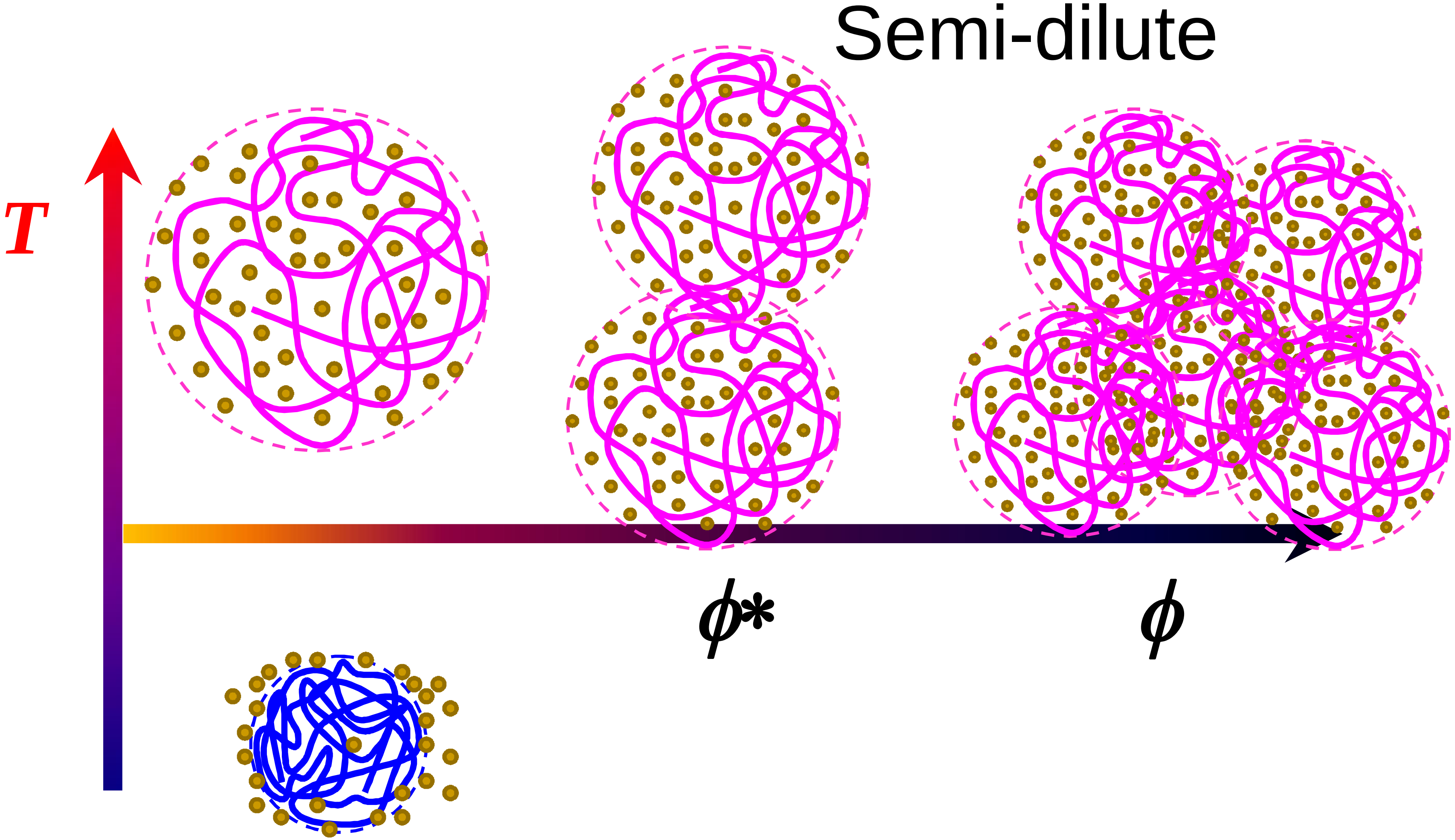
athermal solvents χ**=0** $\chi \ll \frac{1}{2}$ $\chi < \frac{1}{2}$ χ**=1/2** χ**>1/2**



Good solvents **theta(θ)-solvents** **poor solvents**

Excluded Volume **positive** **zero** **negative**

From dilute to concentrated

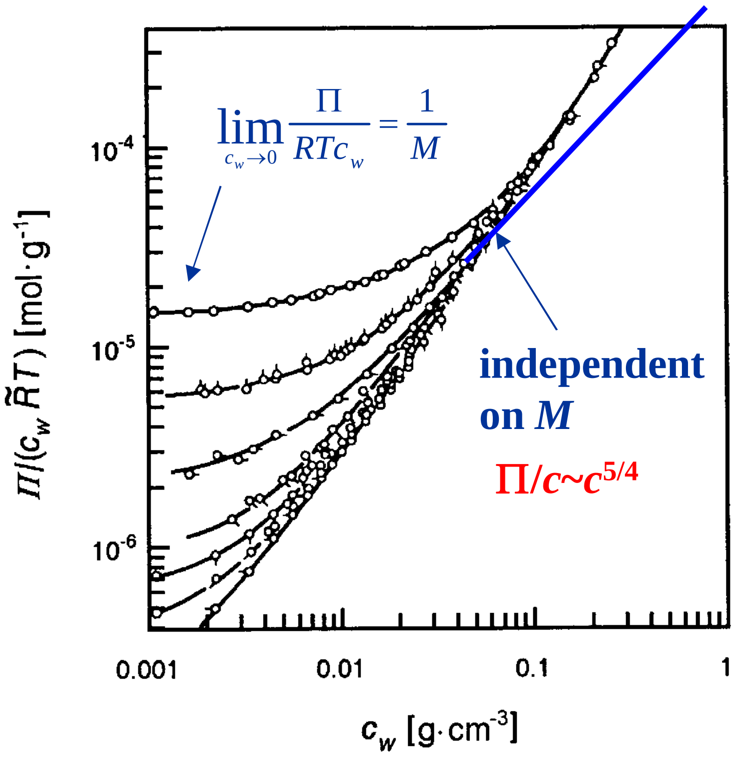


Anomalous phenomenon in Semi-Dilute Polymer Solution

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

$$\phi_2 = \frac{c}{\rho_2} \qquad \rho_2 = \frac{M}{x\bar{V}_1} \qquad \phi_2 = \frac{cx\bar{V}_1}{M}$$

$$\frac{\Pi}{c} = \frac{RT}{\bar{V}_1}\left[\frac{\bar{V}_1}{M} + \left(\frac{1}{2}-\chi\right)\frac{c}{\rho_2^2}\right] = RT\left[\frac{1}{M} + \left(\frac{1}{2}-\chi\right)\frac{c}{\bar{V}_1\rho_2^2}\right]$$



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.)

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

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

$\Pi/c\sim c^{5/4}$??? ✓

需要寻找新的理论手段！

高分子链的重要标度指数

$$\left\langle R_{\mathrm{RW}}^{2}\right\rangle \sim N^{1} \quad \Rightarrow \quad \Phi(\boldsymbol{h},N)=\left(\frac{3}{2\pi N l^{2}}\right)^{3/2}\exp\left(-\frac{3\boldsymbol{h}^{2}}{2Nl^{2}}\right)$$

$$\Downarrow$$

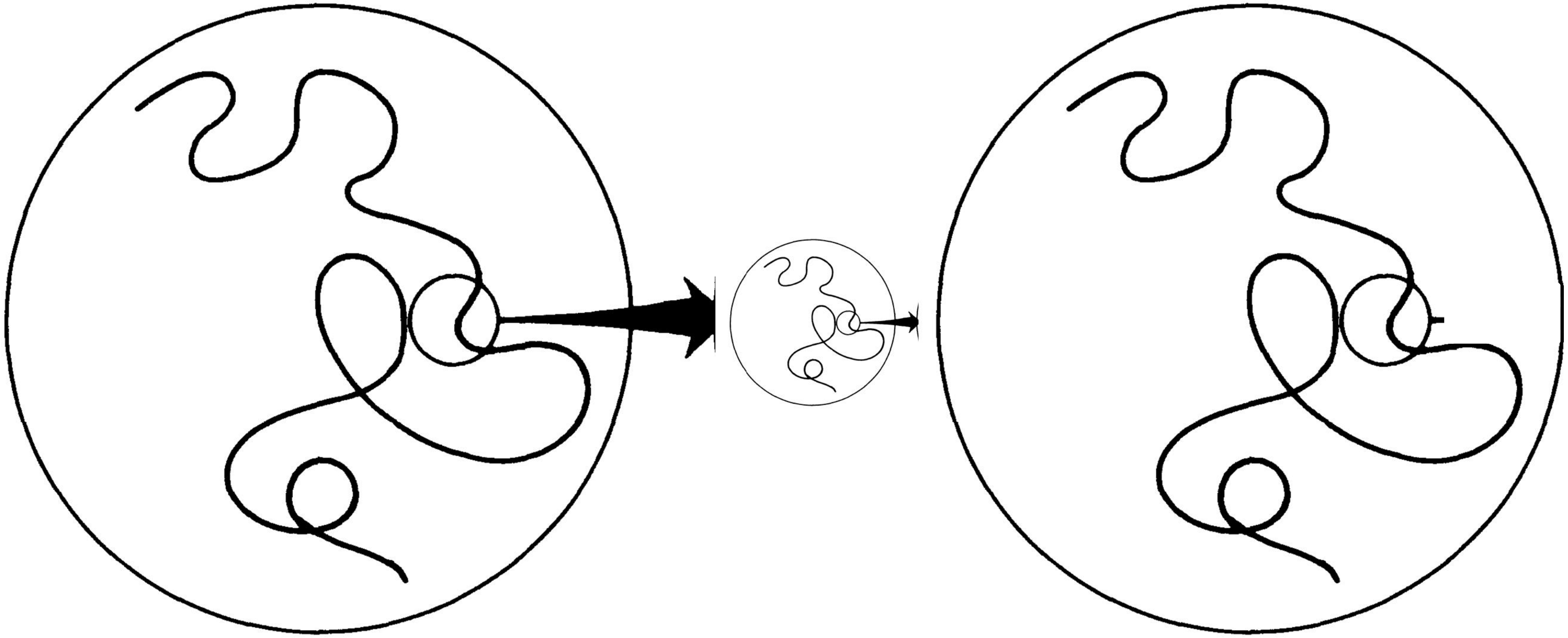
$$\left\langle R_{\mathrm{SAW}}^{2}\right\rangle \sim N^{2\nu} \sim N^{6/5} \quad \Rightarrow \quad ???$$

高分子的绝大多数性质与*Rg*有关

$$\langle \boldsymbol{R_g}\rangle \sim \boldsymbol{N}^{\nu}$$

能否利用*Rg*与*N*的指数去估算高分子的一些重要性质？

自相似与标度律-对高斯链模型的补充

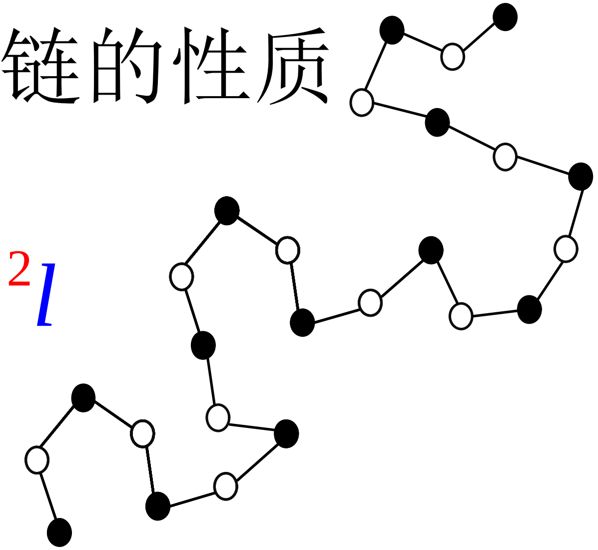


高分子链具有自相似性

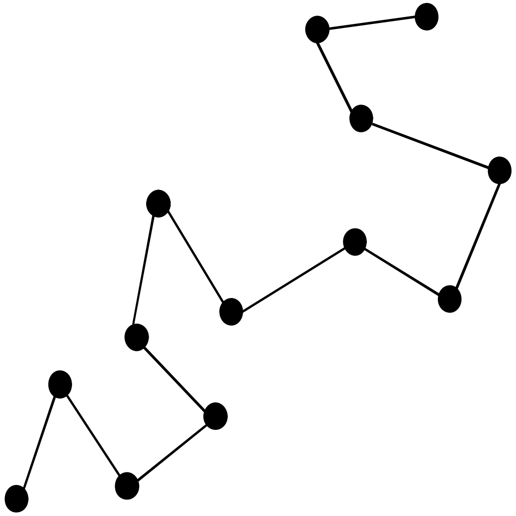
如何利用这个自相似性？？

3.5 Scaling Law(标度律)- (1) 链的性质

(1a) 理想链的性质



$$h \approx N^{1/2} l$$



$$N \to N/g \qquad l \to l\sqrt{g}$$

$$h \approx R_g = F(l, N) \qquad F(l, N) = F(\sqrt{g}\, l, N/g)$$

标度函数：

$$F(l, N) = const. \times \sqrt{g}\, l \left(N/g\right)^{a=1/2} = const. \times \sqrt{N}\, l$$

(1b) 真实链的性质

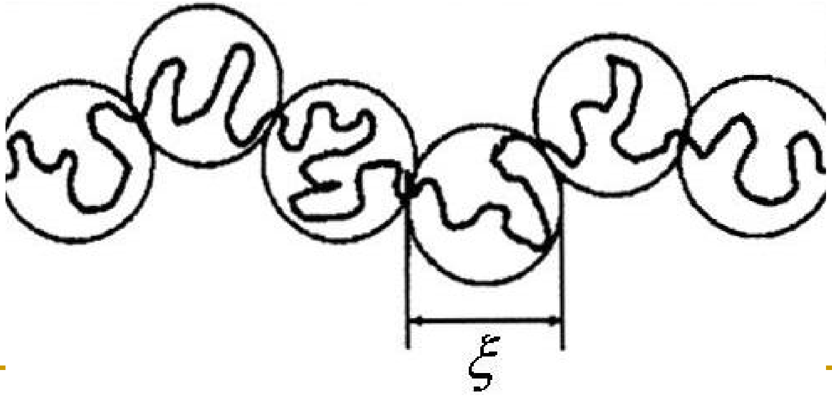
$h \approx N^{\nu} l$

$$N \to N/g \qquad l \to l g^{\nu}$$

$\nu - a = 0,\ a = \nu$

$$h = F\left(l g^{\nu}, N/g\right) = const. \times l g^{\nu} \left(N/g\right)^{a=?} = const. \times N^{\nu} l$$

Blob Model



$\xi \sim g^{\nu} l$

Numbers of blobs: $n = N/g$

Energy of each blob ≈
Thermal fluctuation energy $k_B T$

$$h = F\left(l, N\right) = F\left(\xi, N/g\right)$$

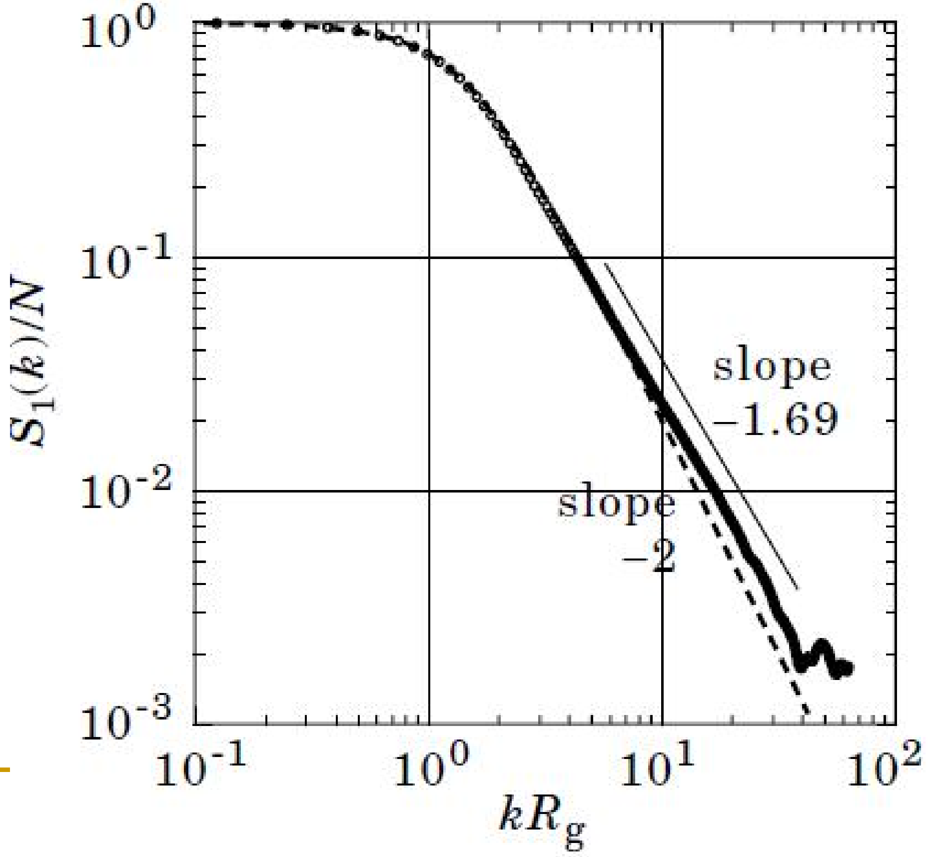
$$G \sim k_B T n = k_B T \frac{N}{g}$$

(2) 高分子链散射函数的标度律

$R_g \sim l$

$$g(\boldsymbol{k}) = Np(\boldsymbol{k}) = \frac{N}{1+\boldsymbol{k}^2\langle R_g^2\rangle/2} = F(kR_g, N) = F(kl, N)$$

l链段长度



(2) 高分子链散射函数的标度律

$$g(\mathbf{k}) = \int \mathrm{d}\mathbf{r}\, \exp(-i\mathbf{k}\cdot\mathbf{r})\,\Psi(\mathbf{r})$$

无量纲

散射矢量 $k \propto 1/\lambda$

$$= F(k, l, N) \propto N$$

大的$\mathbf{k}$，小$\mathbf{r}$部分的贡献大

$$g(\mathbf{k}) = F(kl, N)$$

$$g(\mathbf{k}) \to g(\mathbf{k})/g$$

$$F(klg^{\nu}, N/g) = \frac{1}{g}F(kl, N)$$

如果： $g = N$

$$g(\mathbf{k}) = F(kl, N) = NF(klN^{\nu}, 1) = NF(kR_g)$$

当k很大时，散射函数仅反映了高分子链内部尺度非常小的散射行为在$kR_g >> 1$时，$g(k)$应与N无关

$$a\nu + 1 = 0$$

$$g(\mathbf{k}) = const.\times N(kR_g)^a = const.\times N(klN^{\nu})^a \propto k^a$$

$$a = -1/\nu$$

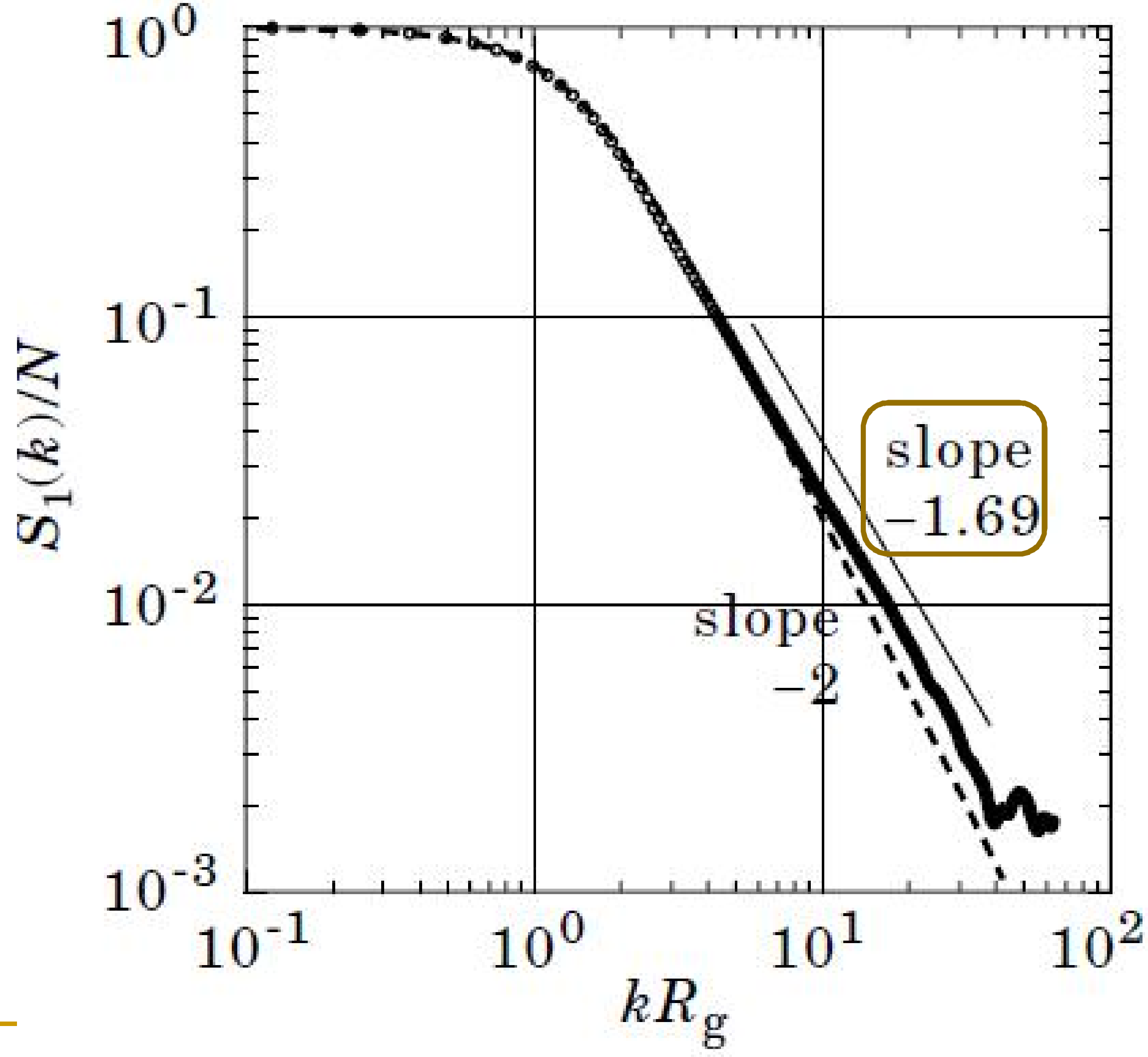
高斯链 $g(\mathbf{k}) = 2N/\mathbf{k}^2\langle R_g^2\rangle \propto k^{-2}$

$|\mathbf{k}|^2\langle R_g^2\rangle >> 1$

ν=1/2 ideal

ν=3/5 real

Form Factor of a Real Chain

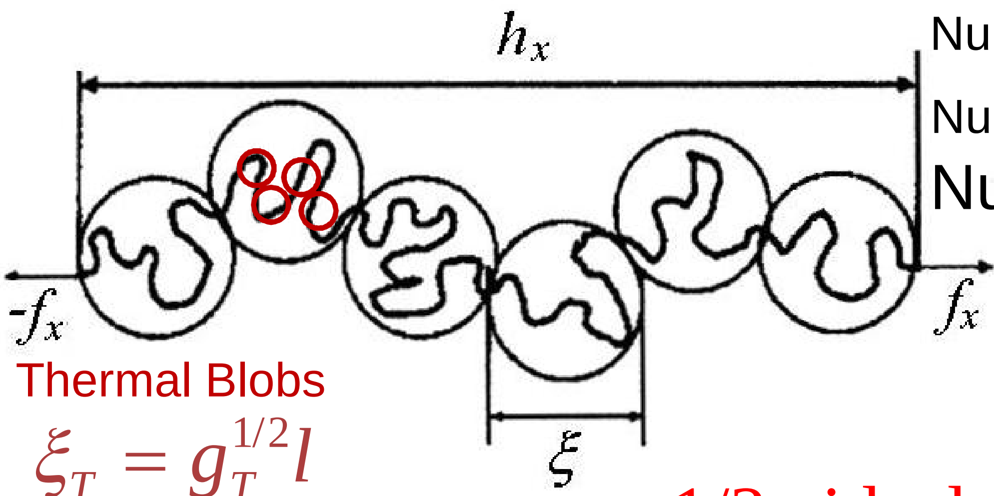


$kR_g >> 1$

$$p(\boldsymbol{k}) \propto k^{-1/\upsilon}$$

$\upsilon = 3/5$

(3) Blob Model - a. Athermal Chain Stretching



Thermal Blobs

$$\xi_T = g_T^{1/2} l$$

Number of Thermal blobs $N_T = N / g_T$

Number of Thermal Blobs in a large blob: g

Number of large blobs: $n=N_T/g$

Energy of one blob ≈ thermal blob ≈ Thermal fluctuation energy k_BT

Total Free Energy: $G \sim k_BT \dfrac{N_T}{g}$

ν=1/2 ideal ν=3/5 athermal

$$\xi \sim g^{\nu} \xi_T$$

$$\boxed{h_x \approx \left(\frac{N_T}{g}\right)\xi}$$

$$g \sim \frac{(N_T\xi_T)^{1/1-\nu}}{h_x^{1/1-\nu}}$$

$$G \sim k_BT\frac{N_T}{g} \boxed{\sim k_BT\left(\frac{h}{N_T^{\nu}\xi_T}\right)^{1/1-\nu}}$$

$$f = \frac{\partial G}{\partial h} \sim k_BT\left(\frac{h^{\nu}}{N_T^{\nu}\xi_T}\right)^{1/1-\nu}$$

由高斯链：

$$f|_{\nu=0.5} \sim k_BT\frac{h}{N_T\xi_T^2}$$

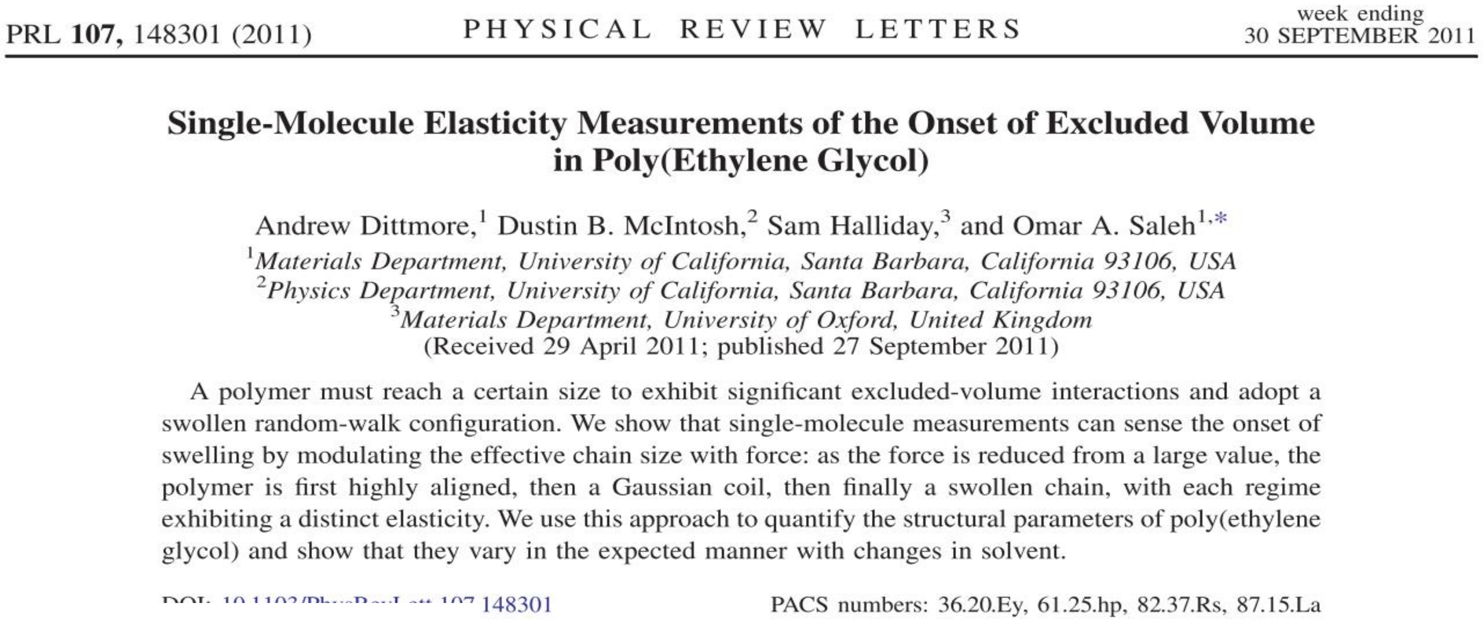
$$\boldsymbol{f} = 3k_BT\frac{\boldsymbol{h}}{N\xi_T^2}$$

非高斯链：

$$f|_{athermal} \sim k_BT\frac{h^{3/2}}{N_T^{3/2}\xi_T^{5/2}}$$

$$\sim k_BT\frac{h^{3/2}}{(N/g_T)^{3/2}\,\xi_T^{5/2}}$$

ν=3/5 thermal solution Energy of large blob $\xi \neq$ thermal blob ξ_T



PRL **107,** 148301 (2011) PHYSICAL REVIEW LETTERS week ending 30 SEPTEMBER 2011

Single-Molecule Elasticity Measurements of the Onset of Excluded Volume in Poly(Ethylene Glycol)

Andrew Dittmore,[1] Dustin B. McIntosh,[2] Sam Halliday,[3] and Omar A. Saleh[1,*]
[1] *Materials Department, University of California, Santa Barbara, California 93106, USA*
[2] *Physics Department, University of California, Santa Barbara, California 93106, USA*
[3] *Materials Department, University of Oxford, United Kingdom*

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A polymer must reach a certain size to exhibit significant excluded-volume interactions and adopt a swollen random-walk configuration. We show that single-molecule measurements can sense the onset of swelling by modulating the effective chain size with force: as the force is reduced from a large value, the polymer is first highly aligned, then a Gaussian coil, then finally a swollen chain, with each regime exhibiting a distinct elasticity. We use this approach to quantify the structural parameters of poly(ethylene glycol) and show that they vary in the expected manner with changes in solvent.

DOI: 10.1103/PhysRevLett.107.148301 PACS numbers: 36.20.Ey, 61.25.hp, 82.37.Rs, 87.15.La

$$f\big|_{\nu=0.6} \sim k_BT\,\frac{h^{3/2}}{(N/g_T)^{3/2}\,\xi_T^{5/2}}$$

$$h \sim f^{2/3}$$

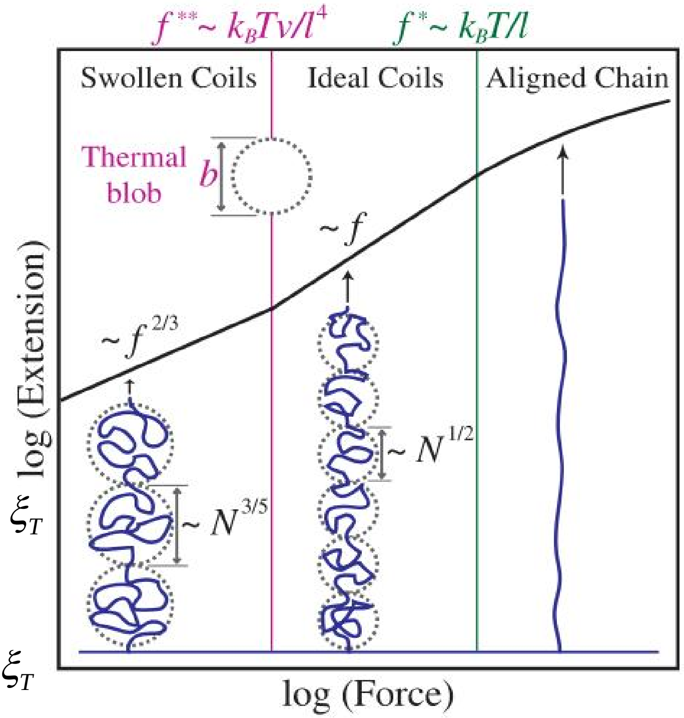
$$f \sim k_BT\,\frac{h^{3/2}}{(N/g_T)^{3/2}\,\xi_T^{5/2}}$$

to

$$f \sim k_BT\,\frac{h}{(N/g_T)\,\xi_T^{2}}$$

$$f^{**} \sim k_BT/\xi_T$$

$$h^{**} \sim (N/g)\,\xi_T$$



$$\xi_T = \left(\frac{u}{l^3}\right)^{-1} l = \frac{l^4}{u}$$

$$f^{**} \sim k_BT/\xi_T$$

$$\xi_T \to l$$

$$f^{*} \sim k_BT/l$$

(b) 真实链的构象(末端距)分布函数

由自由能与末端距的关系: $$G \sim k_B T \left(\frac{h}{N^{\nu} l}\right)^{1/1-\nu}$$

$$\Phi_R(h,N) \sim \exp\left[-\frac{G}{kT}\right] \sim \exp\left(-\alpha\left(\frac{h}{\sqrt{\langle h^2\rangle}}\right)^{1/1-\upsilon}\right)$$

$$h > \sqrt{\langle h^2\rangle} = N^{\upsilon} l$$

$$\Phi_R(h,N) \sim \left(\frac{h}{\sqrt{\langle h^2\rangle}}\right)^{\mu}$$

$$\mu = 0.28$$

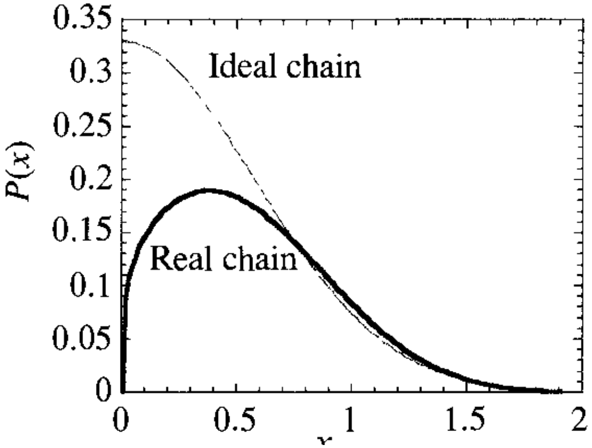
$$h << \sqrt{\langle h^2\rangle}$$

$$\boxed{\Phi_R(x) = 0.278x^{0.28}\exp\left(-1.206x^{2.5}\right)}$$

$$x = h/\sqrt{\langle h^2\rangle}$$

$$\boxed{\Phi_I(x) = \left(\frac{3}{2\pi N l^2}\right)^{3/2} \exp\left(-\frac{3\boldsymbol{h}^2}{2Nl^2}\right)}$$

$$= \left(\frac{3}{2\pi\langle h^2\rangle}\right)^{3/2} \exp(-1.5x^2)$$

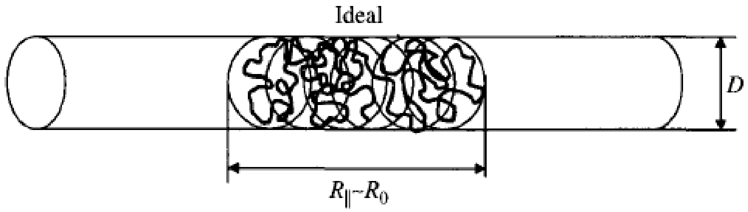


(2) Blob Model – c. Biaxial Compression

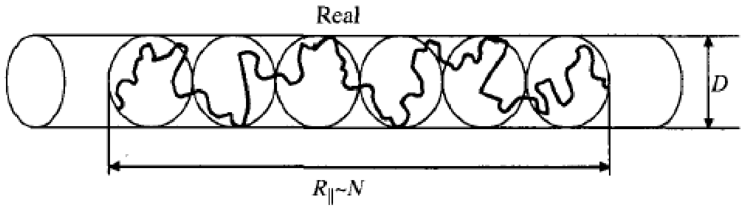
$D = g^{\nu} l$ or $D = g^{\nu} \xi_T$

ν=1/2 ideal

ν=3/5 athermal



$$R_{//}\Big|_{ideal} \sim \left(\frac{N}{g}\right)^{1/2} D \sim \left(\frac{N l^2}{D^2}\right)^{1/2} D \approx N^{1/2} l$$



$$R_{//}\Big|_{real} \sim \left(\frac{N}{g}\right) D \sim \left(\frac{N l^{1/\nu}}{D^{1/\nu}}\right) D \sim \boxed{N} l \left(\frac{l}{D}\right)^{2/3}$$

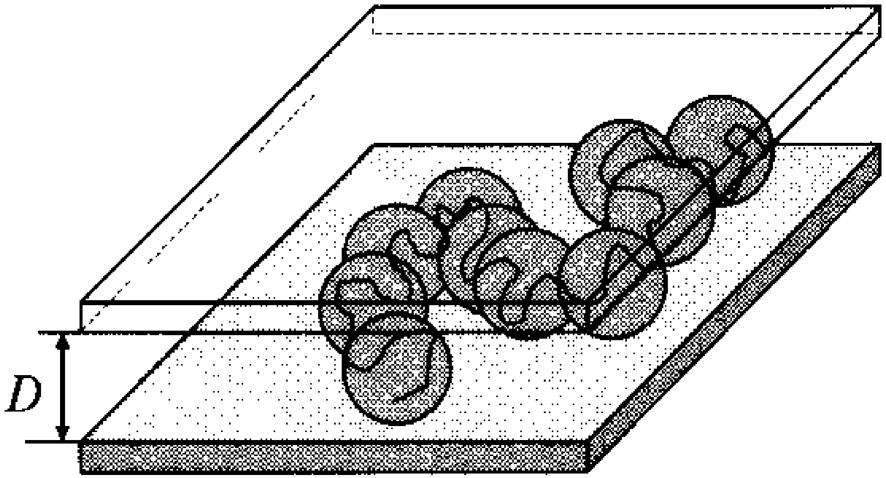
$$G_{conf}\Big|_{ideal} = k_B T \frac{N}{g} = \boxed{k_B T N \left(\frac{l}{D}\right)^2} = k_B T \left(\frac{R_0}{D}\right)^2$$

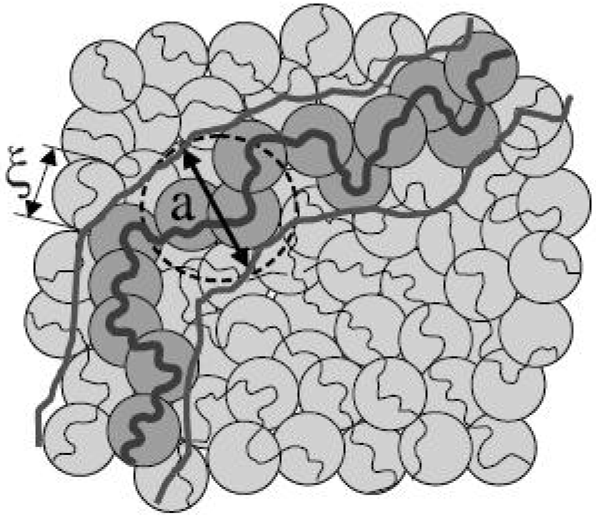
$$R_0 \approx N^{1/2} l$$

$$G_{conf}\Big|_{real} = k_B T \frac{N}{g} = \boxed{k_B T N \left(\frac{l}{D}\right)^{1/\nu}} = k_B T \left(\frac{N^{\nu} l}{D}\right)^{1/\nu} = k_B T \left(\frac{R_r}{D}\right)^{5/3}$$

$$R_r \approx N^{3/5} l$$

d. Uniaxial compression ??





$$G_{conf} = k_B T \frac{R^2}{Nl^2} = k_B T \frac{R^2}{R_0^2}$$

Entropy of an ideal chain

$$G_{conf,blob} = k_B T \frac{R^2}{(N/g)D^2}$$

Entropy of an ideal blob chain

$$G_{\mathrm{int}} = k_B T u \frac{N^2}{R^3}$$

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

$$G_{\mathrm{int},blob} = k_B T D^2 \frac{(N/g)^2}{R^2}$$

Interaction between blobs

$$\frac{\partial \left(G_{conf,blob} + G_{\mathrm{int},blob} \right)}{\partial R} = 0$$

Answers：

$$R_{real,d} \approx N^{\frac{3}{d+2}} l$$

d: dimensions (空间维度)

$$R_{//} \approx N^{3/4} l$$

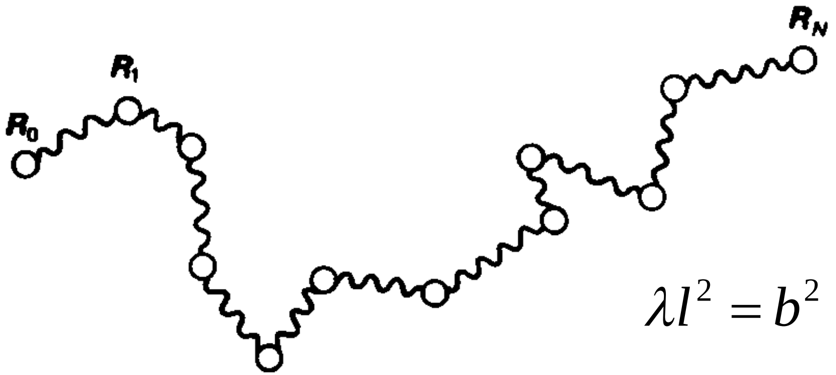
$$R_{ideal} \approx N^{\frac{1}{2}} l$$

高分子物理中的理论方法I

1. 高斯链模型

$$\left\langle R_{\mathrm{RW}}^2 \right\rangle \sim N^1$$

$$\boxed{\Phi(\boldsymbol{h}, N_g) = \left(\frac{3}{2\pi N_g l_g^2}\right)^{3/2} \exp\left(-\frac{3\boldsymbol{h}^2}{2N_g l_g^2}\right)} \Longleftrightarrow \boxed{\frac{\partial \Phi(\boldsymbol{h}, N_g)}{\partial N} = \frac{l_g^2}{6}\frac{\partial^2 \Phi(\boldsymbol{h}, N_g)}{\partial \boldsymbol{h}^2}}$$



$$\lambda l^2 = b^2$$

$$\Psi\left(\{\boldsymbol{h}_i\}\right) = \prod_{i=1}^{N_g}\left(\frac{3}{2\pi\lambda l^2}\right)^{3/2} \exp\left(-\frac{3\boldsymbol{h}_i^{\,2}}{2\lambda l^2}\right)$$

$$= \left(\frac{3}{2\pi b^2}\right)^{3N_g/2} \exp\left(-\sum_{n=1}^{N_g}\frac{3\left(\boldsymbol{R}_i - \boldsymbol{R}_{i-1}\right)^2}{2b^2}\right)$$

$$\boxed{= const \exp\left[-\frac{3}{2b^2}\int_0^{N_g}\left(\frac{\partial \boldsymbol{R}_n}{\partial n}\right)^2 dn\right]}$$

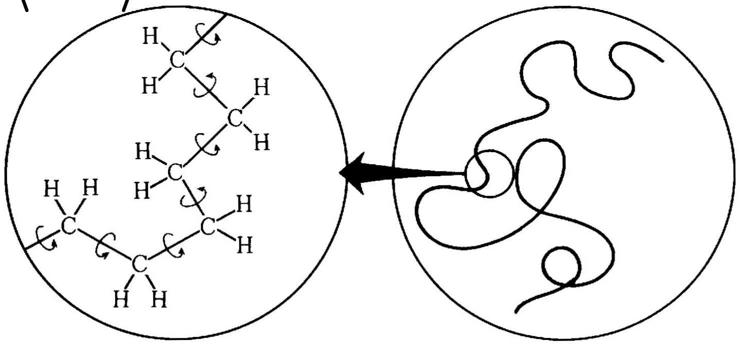
Path Integral(路径积分)

Edward’s Minimum Model

$\Psi\left(\{\boldsymbol{h}_i\}\right) + \text{interaction energy} \Rightarrow H$ 哈密顿量 $\Rightarrow$ Mean-field Free Energy

高分子物理的主线-高斯链模型

$$\left\langle R^2 \right\rangle \sim N^{2\nu} l^2$$



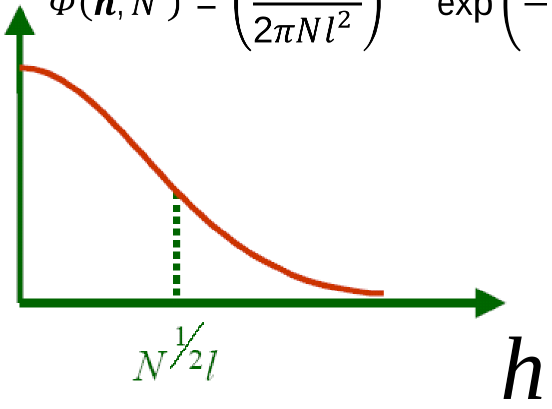
In θ solution:

$$\left\langle R^2 \right\rangle_0 = \alpha N l^2 \qquad \boxed{\left\langle R^2 \right\rangle_0 = l_e L}$$

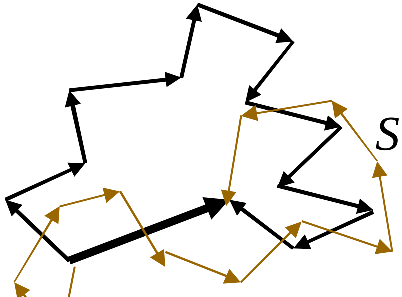
Gaussian Chain Model

$$\Phi\left(h\right)$$

$$\Phi(\mathbf{h}, N) = \left(\frac{3}{2\pi N l^2}\right)^{3/2} \exp\left(-\frac{3\mathbf{h}^2}{2Nl^2}\right)$$



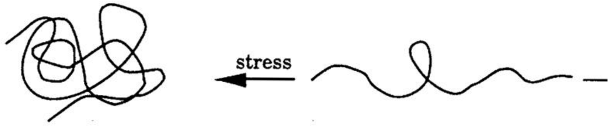
Entropy of Chain Conformations



$$S_{conf}(\mathbf{h}, N_g) = -\frac{3}{2} k_B \frac{\mathbf{h}^2}{N_g l^2} + C$$

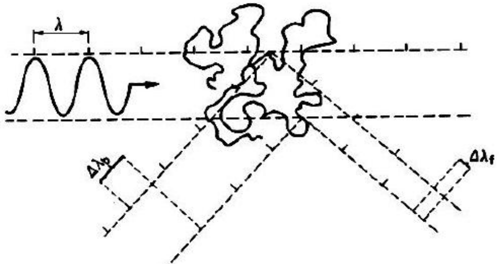
$\mathbf{h}$, $\Phi(\mathbf{h}, N)$

Mechanic Properties



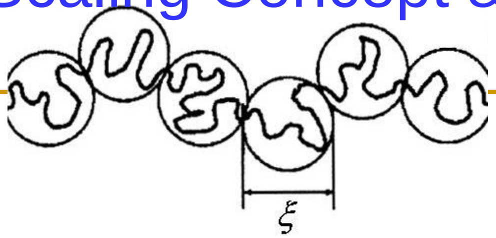
$$\boldsymbol{f} = 3k_B T \frac{\mathbf{h}}{Nl^2}$$

Scattering Theory ($R > \lambda/20$)



$$\boxed{p(\mathbf{k}) = \frac{1}{1 + \mathbf{k}^2 \left\langle R_g^2 \right\rangle / 2}}$$

Scaling Concept & Blob Model



$$G \sim k_B T \frac{N}{g}$$

高分子物理中的理论方法II

标度律是高斯链模型的补充，尤其适用于真实链

$$\left\langle R_{\mathrm{SAW}} \right\rangle \sim N^{\nu} \sim N^{3/5}$$

根据变量$(N,l,\boldsymbol{k})$和量纲分析设计标度函数

利用降低分辨率时的标度不变性和量纲之间的关系，考察物理性质与变量的关联

结合blob model考察物理性质与变量的关联

2 Unique Features of Polymers

Thermodynamics:

(1) Large Spatial Extent

(2) Connectivity

- **a. Tacticity – 立构性**
- **b. Polymer Topology**
- **c. Flexible vs. Rigid**
- **d. Multiple Confirmations (Entropy)**

(3) Multiple Interactions (Enthalpy)

Dynamics:

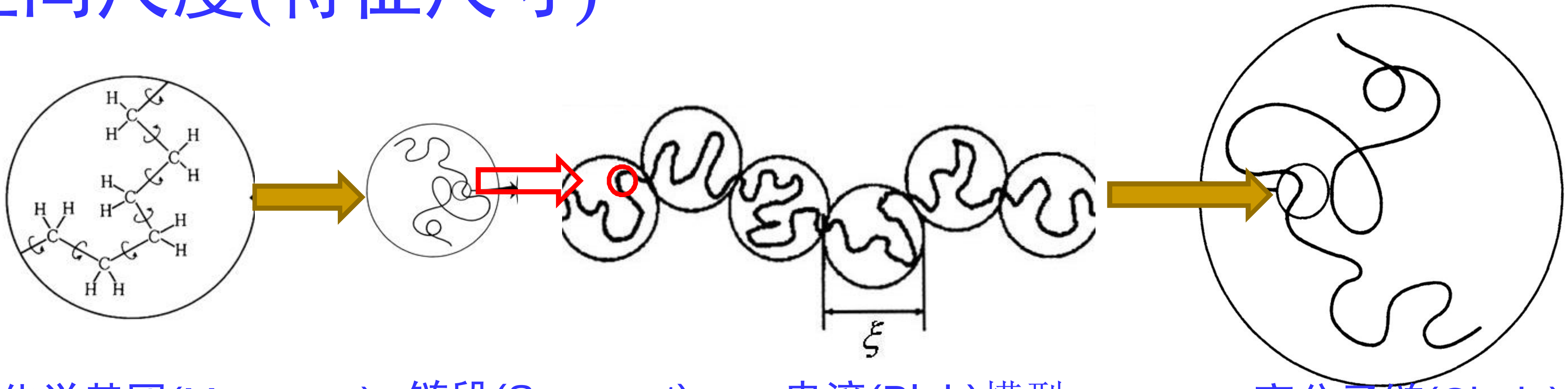
(4) Entanglement

(5) Responsive Molecules

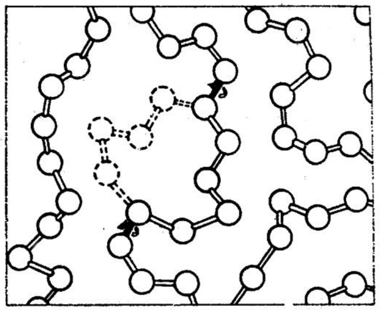
- **a. Large-scale Relaxation Time Spectrum**
- **b &c . Temp, Rate and Time Dependent Behavior**

Spatial Extent & Connectivity

空间尺度(特征尺寸)



化学基团(Monomer) 链段(Segment) 串滴(Blob)模型 高分子链(Chain)



多链聚集态

Entropy

Multiple Confirmations (Entropy)

A Chain $S_{conf} \approx -k_B \frac{\boldsymbol{R}^2}{Nl^2}$ A Blob Chain $S_{conf} \approx -k_B \frac{\boldsymbol{R}^2}{(N/g)\xi^2}$

Flory-Huggins Entropy of Mixing for Multi Chains

$$\Delta S_{mixing} = -k_B\left[N_1 \ln\phi_1 + N_2 \ln\phi_2\right] = -k_B \frac{V_m}{\bar{V}_s}\left[\frac{\phi_1}{x_1}\ln\phi_1 + \frac{\phi_2}{x_2}\ln\phi_2\right]$$

Enthalpy

Multiple Interactions (Enthalpy)

Two-body interaction

within a Blob $\bar{E} \approx k_B T |u| \frac{g_T^2}{\xi_T^3}$

In a 3d Chain $H_{2,\mathrm{int}} = k_B T u \frac{N^2}{R^3}$ In a 3d Blob Chain $H_{2,\mathrm{int}} = k_B T \xi^3 \frac{(N/g)^2}{R^3}$

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

2d chain $H_{2,\mathrm{int}} = k_B T u \frac{N^2}{R^2}$ 2d Blob Chain $H_{2,\mathrm{int}} = k_B T \xi^2 \frac{(N/g)^2}{R^2}$

$$u = s_c (1 - 2\chi) \approx s_c \tau \quad s_c \approx l^2$$

Flory-Huggins Enthalpy of Mixing for Multi Chains $\Delta H_{mixing} = \frac{V_m}{\bar{V}_s} k_B T \chi \phi_1 \phi_2 = k_B T \chi x N_2 \phi_1$

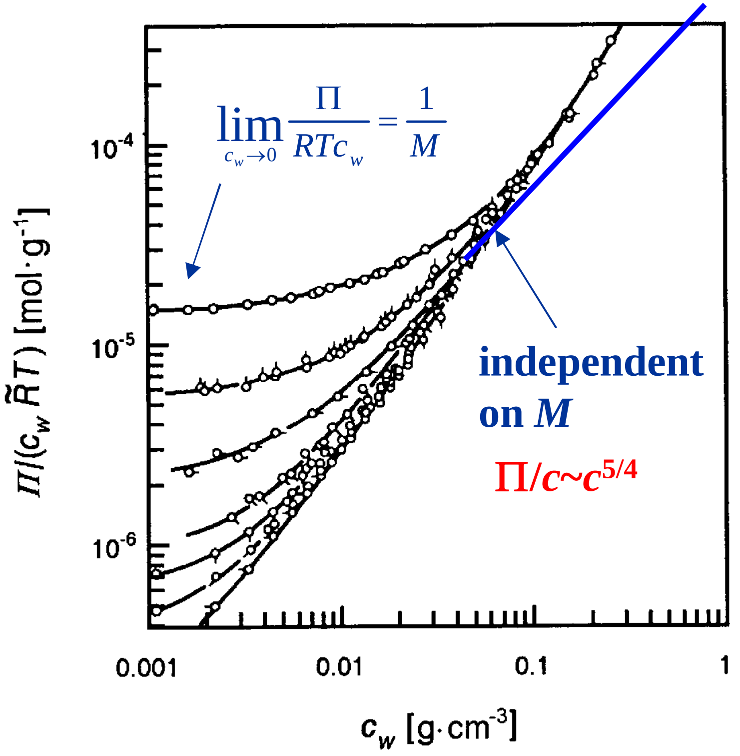
Three-body

3d $H_{3,\mathrm{int}} / k_B T = w \phi_2^3 R^3 = w \frac{N^3}{R^6}$

3.6 Semi-dilute Solutions of Polymers

$$\Pi = \frac{RT}{\bar{V}_1}\left[\frac{1}{x}\phi_2 + \left(\frac{1}{2}-\chi\right)\phi_2^2\right] \qquad \phi_2 = \frac{c}{\rho_2} \qquad \rho_2 = \frac{M}{x\bar{V}_1} \qquad \phi_2 = \frac{cx\bar{V}_1}{M}$$

$$\frac{\Pi}{c} = \frac{RT}{\bar{V}_1}\left[\frac{\bar{V}_1}{M} + \left(\frac{1}{2}-\chi\right)\frac{c}{\rho_2^2}\right] = RT\left[\frac{1}{M} + \left(\frac{1}{2}-\chi\right)\frac{c}{\bar{V}_1\rho_2^2}\right]$$



Osmotic pressure measured for samples of poly(α-methylstyrene) dissolved in toluene (25 °C). Molecular weight vary between *M* = 7 × 10^4 (uppermost curve) and *M* = 7.47 × 10^6 (lowest curve). (Noda,I.; et al. *Macromolecules* **1981**, *14*, 668.)

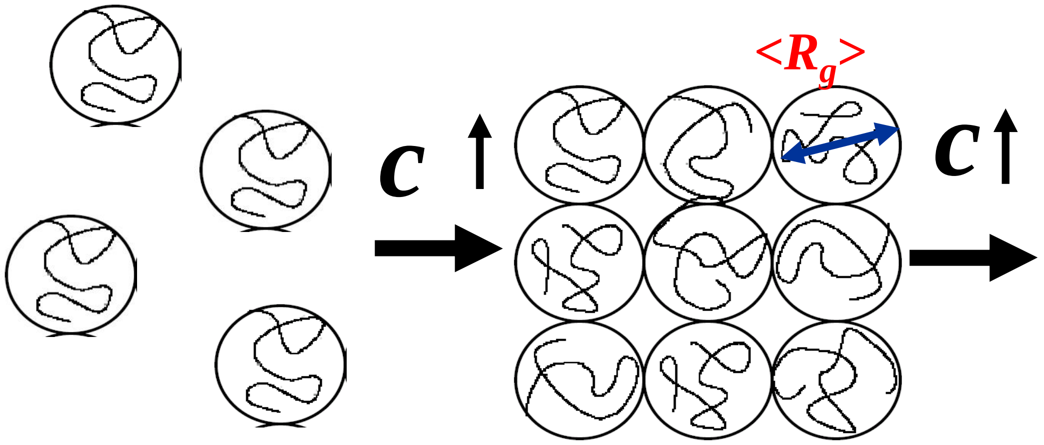
$$\phi_2 \ll 1 \qquad \phi_2^2 \gg \phi_2/x$$

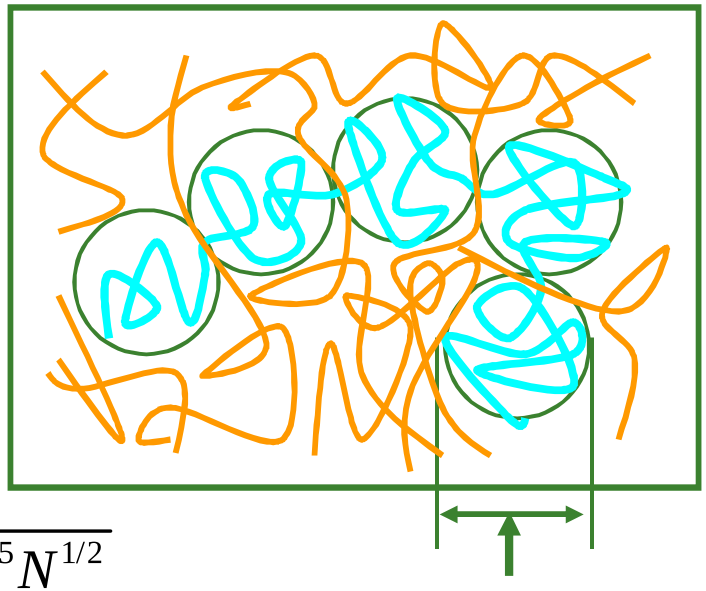
$$\Pi/c \sim c^0 \qquad \xcancel{\Pi/c \sim c^1}$$

$$\Pi/c \sim c^{5/4}$$ ✓

(1) overlap concentration *c**

dilute *c*: < *c**   **Overlap concentration: *c* = *c****   **Semi-dilute regime: *c* > *c****





$$\phi^* = \frac{Nl^3}{\langle R_g \rangle^3} \sim \frac{N}{N^{3\upsilon}\tau^{3/5}} \sim \frac{1}{N^{3\upsilon-1}\tau^{3/5}} \approx \frac{1}{N^{3\upsilon-3/2}\tau^{3/5}N^{1/2}}$$

$$\approx \frac{1}{\alpha^3 N^{1/2}} \qquad \boxed{\sim N^{-4/5}\tau^{-3/5}} \qquad c^* = \phi^* \rho_2$$

Apparent correlation length

(表观相关长度) $R_g > \xi_{app} > \xi_T > l$

For good solvent, $v = 3/5$

$$\tau = 1 - 2\chi = 1 - \frac{\chi}{1/2} = \left(1 - \frac{T_\theta}{T}\right) \quad \boxed{R_g \propto N^{\nu}\left(1-2\chi\right)^{1/5} l = N^{\nu}\tau^{1/5} l} \quad \alpha = \frac{\langle R_g \rangle}{\langle R_0 \rangle} = N^{\upsilon-1/2}\tau^{1/5}$$

(2) Osmotic pressure of semi-dilute solution

Van’t Hoff relation of osmotic pressure

$$\frac{\Pi}{c} \approx \frac{RT}{M} f\left(c\right)$$

$$\Pi = RT\left[\frac{c}{M} + \left(\frac{1}{2} - \chi\right)\frac{c^2}{\bar{V}_1 \rho_2^2}\right]$$

osmotic pressure from Flory-Huggins Theory

$$\rho_2 \simeq \frac{M}{x\bar{V}_1} \qquad \bar{V}_1 = \tilde{N} v_c$$

$$= RT\left[\frac{c}{M} + \left(\frac{1}{2} - \chi\right)\frac{x^2 \bar{V}_1}{M^2} c^2\right] = RT\left[\frac{c}{M} + \frac{c^2}{M^2}\left(\frac{1}{2} - \chi\right)\tilde{N} v_c x^2\right]$$

$$u = v_c\left(1 - 2\chi\right)$$

$$\sum_{i=1}^{x} i = \frac{x^2}{2}$$

$$= RT\left[\frac{c}{M} + \tilde{N}\left(\frac{c}{M}\right)^2 x^2 \frac{u}{2}\right] = RT\left[\frac{c}{M} + \tilde{N}\left(\frac{c}{M}\right)^2 u \sum_{i=1}^{x} i\right]$$

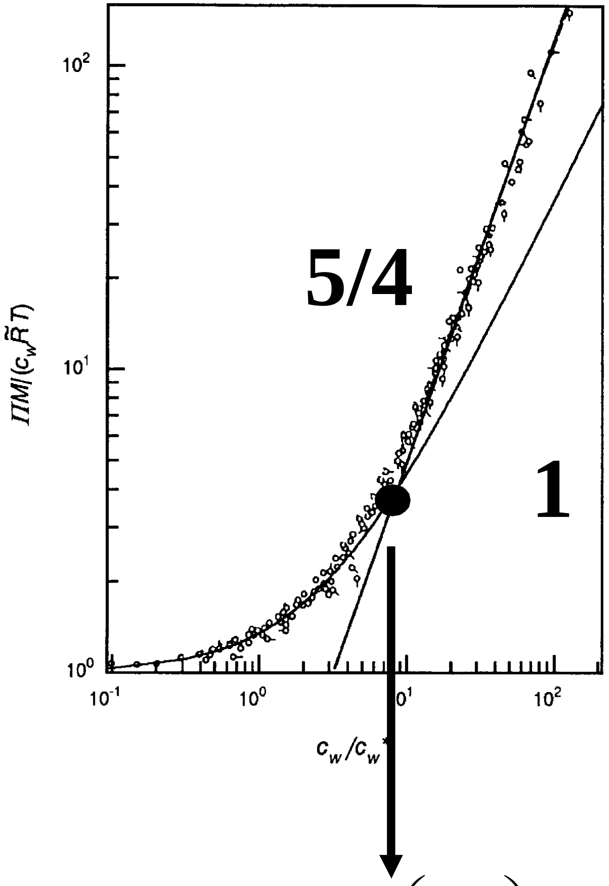
$$u\sum_{i=1}^{x} i \approx U = R_g^3$$

$$\approx RT\left[\frac{c}{M} + \left(\frac{c}{M}\right)^2 \tilde{N} R_g^3\right] \qquad = RT\,\frac{c}{M}\left[1 + c\,\frac{\tilde{N} R_g^3}{M} + \cdots\right]$$

$$c^* = \frac{M}{R_g^3}$$

$$= RT\,\frac{c}{M}\left[1 + B\left(\frac{c}{c*}\right) + B'\left(\frac{c}{c*}\right)^2 + \ldots\right] \qquad \boxed{\Pi = \frac{c}{M} RTf\left(\frac{c}{c*}\right)} = \frac{c}{M} RT\left(\frac{c}{c*}\right)^m$$

Scaling Law of semi-dilute solution



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

- **Osmotic pressure:**

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

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

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

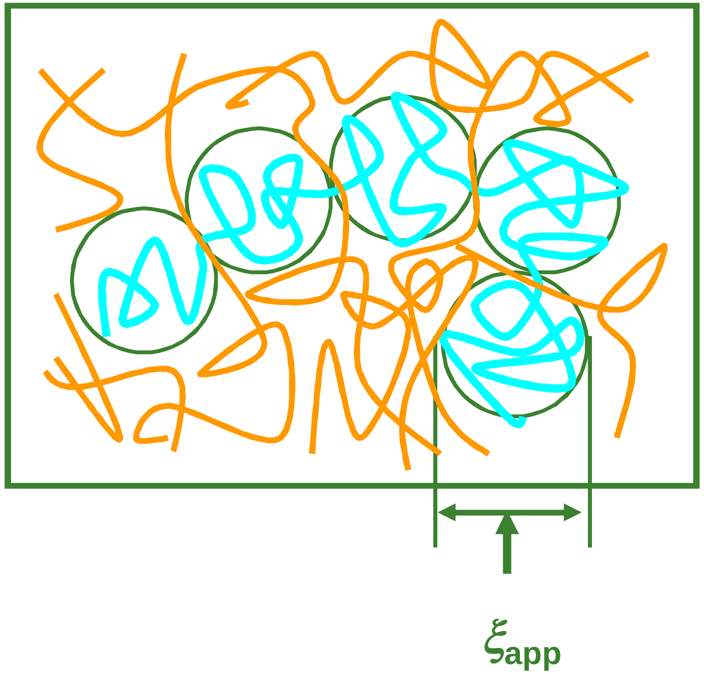
$$m(3\nu - 1) - 1 = 0$$

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

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

$$c^2 < \Pi < c^3$$

(3) Apparent correlation length ξ_{app}:



$$\xi_{app} = R_g\, f\left(\frac{c}{c^*}\right)$$

$$\xi_{app} \propto N^{\nu} l \tau^{1/5} \left(\frac{c}{c^*}\right)^m \quad \begin{cases} \propto R_g = N^{\nu} l & (c = c^*) \\ \propto N^{\nu} c^m N^{m(3\upsilon-1)} \tau^{(1+3m)/5} l & (c \geq c^*) \end{cases}$$

$$c^* \propto N^{1-3\nu} \tau^{-3/5}$$

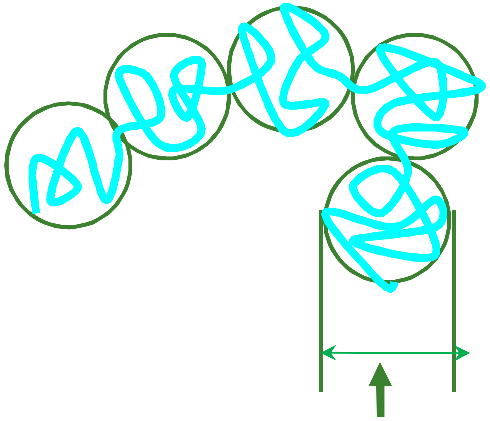
ξ_{app} is independent on *N*:

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

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

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

(4) Polymer Shapes in Semi-dilute Solutions



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

blob model:
由N/g个串滴单元组成的理想链

$$\langle R_g^2 \rangle = (N/g)\,\xi_{app}^2$$

串滴内- 由g个单元组成的扩张(良溶剂下)的短链

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

串滴内有g个链段单元, 串滴数N/g, 每个串滴大小ξ_{app}

$$\xi_{app} \sim g^{3/5}\tau^{1/5} l \quad \longrightarrow \quad c \sim g l^3 / \xi_{app}^3$$

证明串滴内外浓度均匀

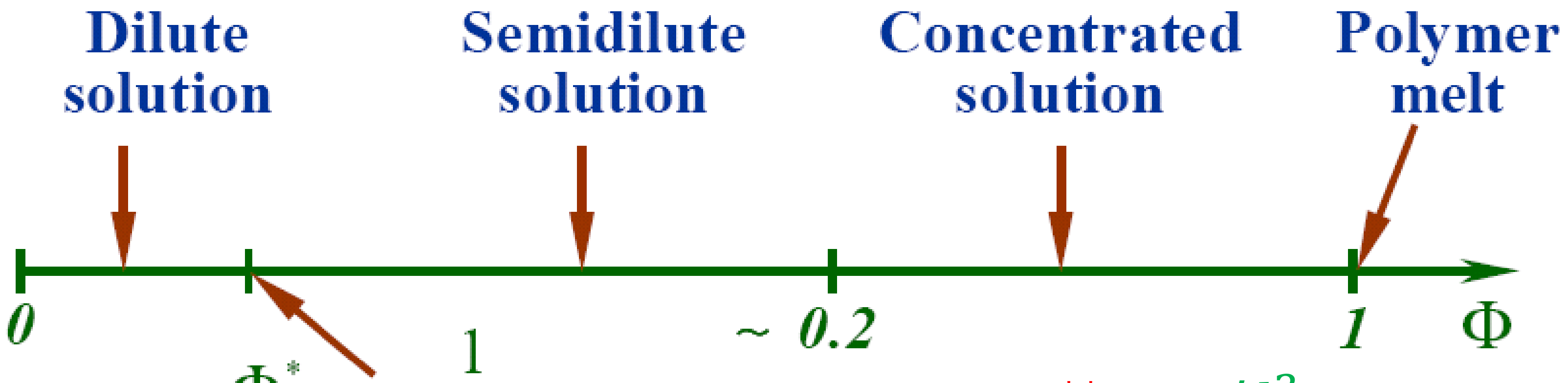
$\xi_{app} \sim c^{-3/4}\tau^{-1/4} l$

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

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

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

$$\langle R_g^2 \rangle_{\text{semi-dilute}} \sim N c^{-1/4}\tau^{1/4} l^2$$ Gaussian Chain



Dilute solution

Semidilute solution

Concentrated solution

Polymer melt

$$\Phi^* \propto \frac{1}{\alpha^3 N^{1/2}} \qquad \alpha = \frac{R_g}{R_0}$$

溶胀因子

$$\Phi^{**} \propto u/l^3$$

$$\xi_{\text{app}} >> R_g \qquad \xi_{\text{app}} \leq R_g \qquad \xi_{\text{app}} \sim u << R_g$$

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

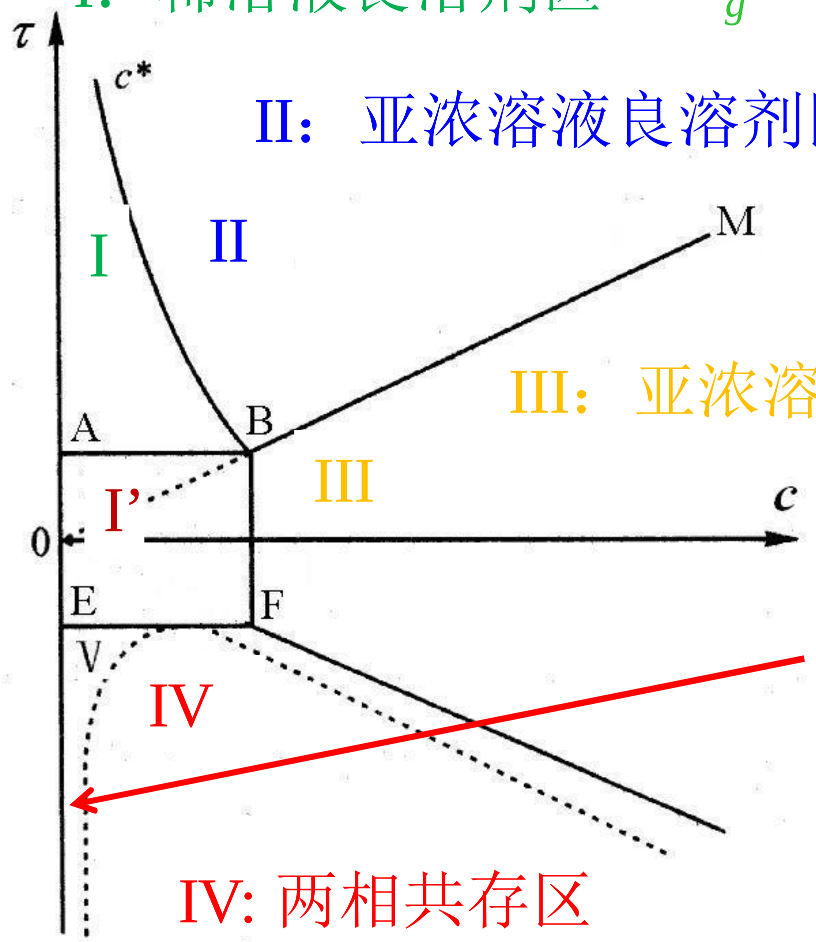
The presence of monomers from the other chains begins to "screen" (屏蔽) the intramolecular excluded volume interactions.

实质

亚浓溶液: 大串滴在溶液中的分布达到均匀, 链段分布未达均匀

浓溶液: 小串滴在溶液中的分布完全均匀

(5) 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: $c^* = N^{-4/5}\tau^{-3/5}$

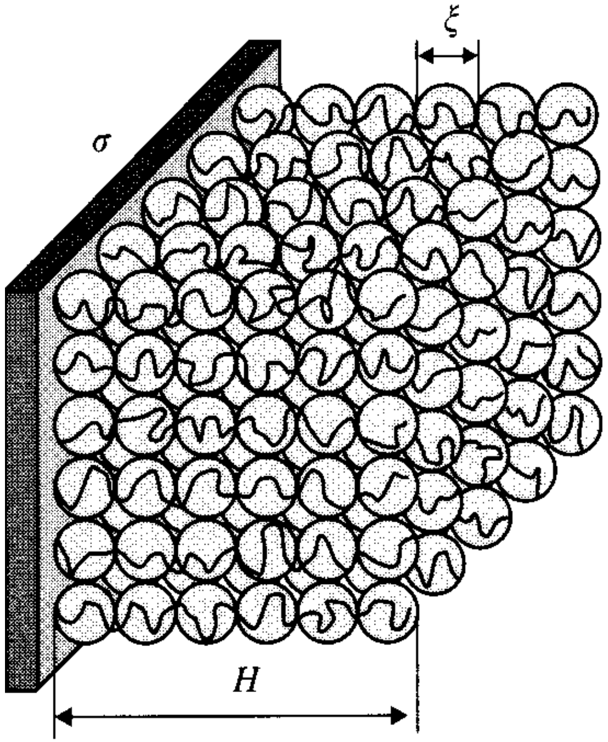
BM 方程：$c = \tau$

AB 方程：$\tau = N^{-1/2}$

EF 方程：$\tau = -N^{-1/2}$

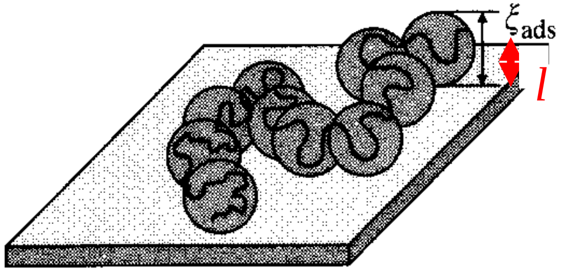
Other Interesting Topics:

Grafted Layer

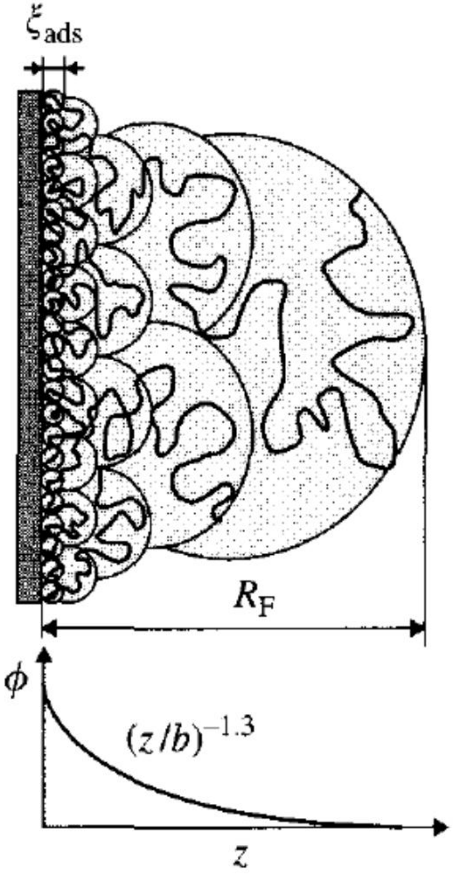


Adsorption:

from Single Chain



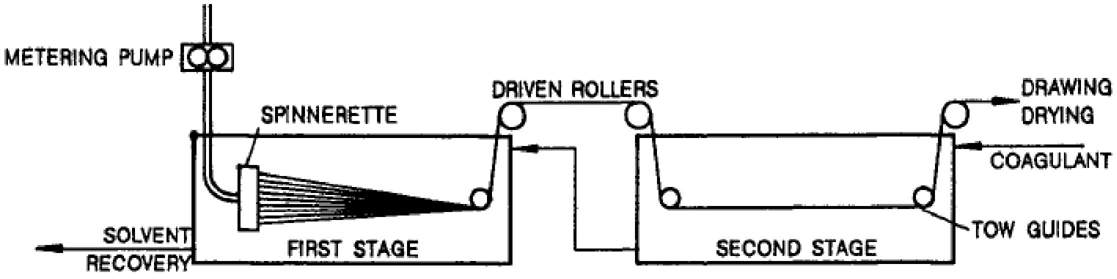
to Multichain

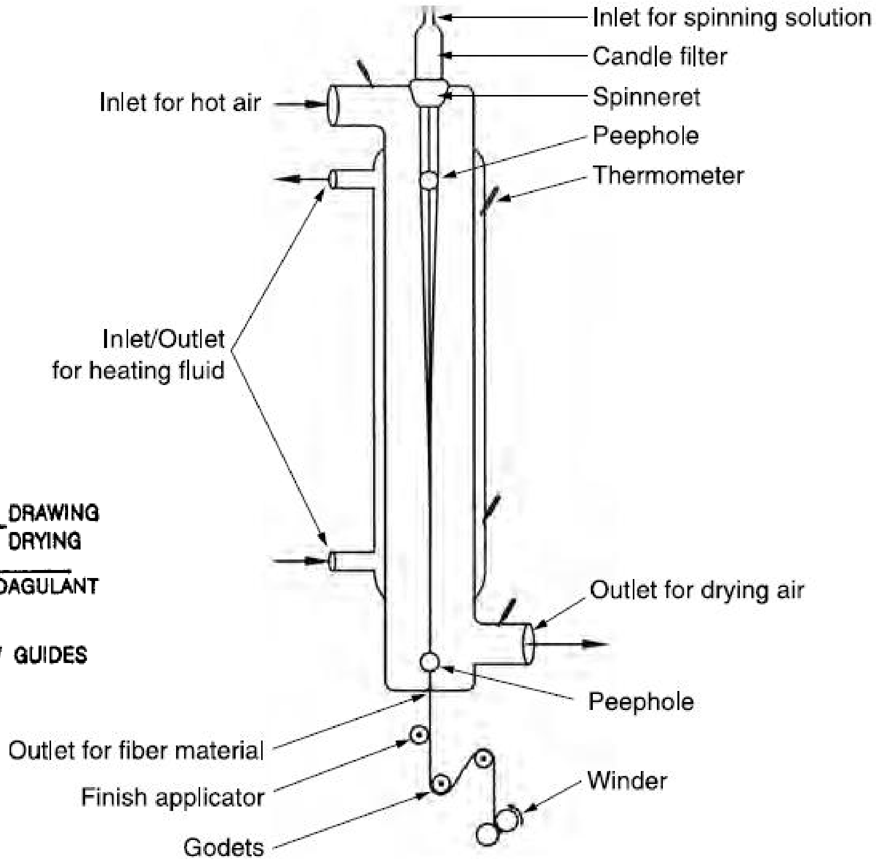


(6) Concentrated Solutions

1. Polymer-Plasticizer
2. Spinning Solution
3. Gel

Fiber Spinning



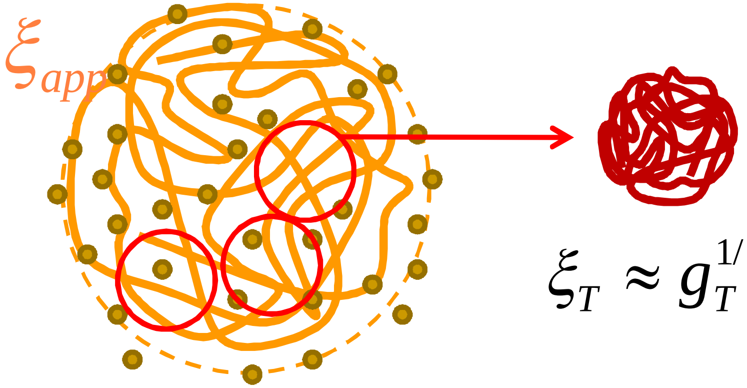


Wet Spinning

Dry Spinning

(6) Concentrated Polymer Solutions

Concentrated regime c^{**}



$$\xi_T \approx g_T^{1/2} l$$

$$R \propto \xi_T \left(\frac{N}{g_T}\right)^{\frac{3}{5}} \simeq g_T^{1/2} \left(\frac{N}{g_T}\right)^{\frac{3}{5}} l = g_T^{-\frac{1}{10}} N^{\frac{3}{5}} l$$

$$\boxed{= N^{3/5} \left(\frac{u}{l^3}\right)^{1/5} l}$$

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

$$v_c \approx l^3$$

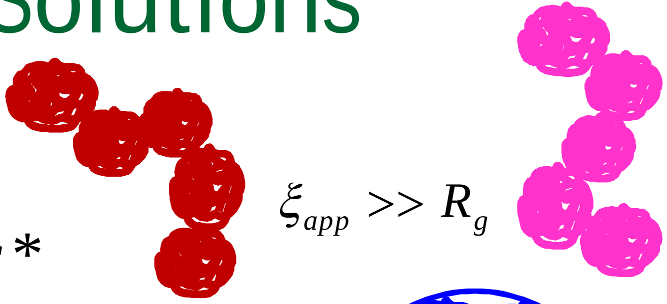
$$g_T \approx \left(\frac{u}{l^3}\right)^{-2}$$

$$\xi_T \approx \left(\frac{u}{l^3}\right)^{-1} l \approx \tau^{-1} l$$

$$\bar{E} \approx k_B T g_T^2 \frac{|u|}{\xi_T^3} \approx k_B T$$

Dilute

$c < c^*$

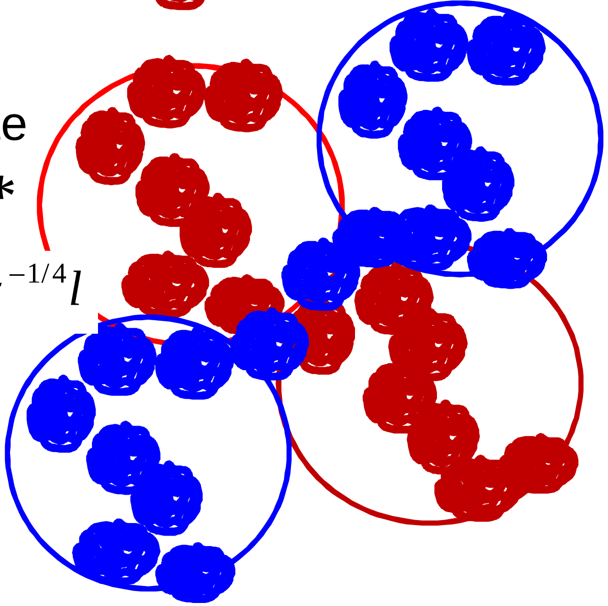


$\xi_{app} >> R_g$

Semi-dilute

$c > c^*$

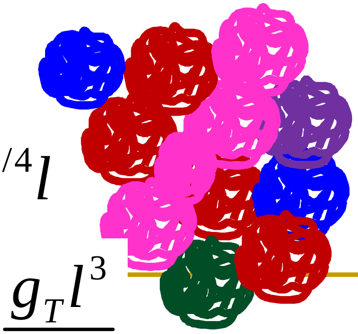
$\xi_{app} \propto c^{-3/4} \tau^{-1/4} l$



Concentrated

$c > c^{**}$

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



$= \xi_T$

$$c^{**} \approx \tau = \frac{u}{l^3} = \frac{g_T l^3}{\xi_T^3}$$

(7) Polymer Melts

Polymer A + Solvent B

$$\Pi = \frac{kT}{v_c}\left[\frac{\phi_A}{N_A} + (1-2\chi)\frac{\phi_A^2}{2} + \cdots\right]$$

$c_A = \phi_A / v_c$ 单体A的质量浓度

Excluded Volume

$$\Pi = kT\left[\frac{c_A}{N_A} + (1-2\chi)v_c\frac{c_A^2}{2} + \cdots\right]$$

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

Polymer A + Polymer B

$$\chi = 0$$

$$\Pi = kT\left[\frac{c_A}{N_A} + \left(\frac{1}{N_B} - 2\chi\right)v_c\frac{c_A^2}{2} + \cdots\right]$$

$$u = v_c\left(\frac{1}{N_B} - 2\chi\right)$$

$$u = \frac{v_c}{N_B} \approx \frac{l^3}{N_B}$$

$$\xi_T \approx l g_T^{1/2}$$

$$\bar{E} \approx k_B T g_T^2 \frac{u}{\xi_T^3}$$

$$\approx k_B T \frac{u}{l^3}\frac{g_T^2}{g_T^{3/2}} \approx k_B T$$

$$g_T \approx \frac{l^6}{u^2} \approx N_B^2$$

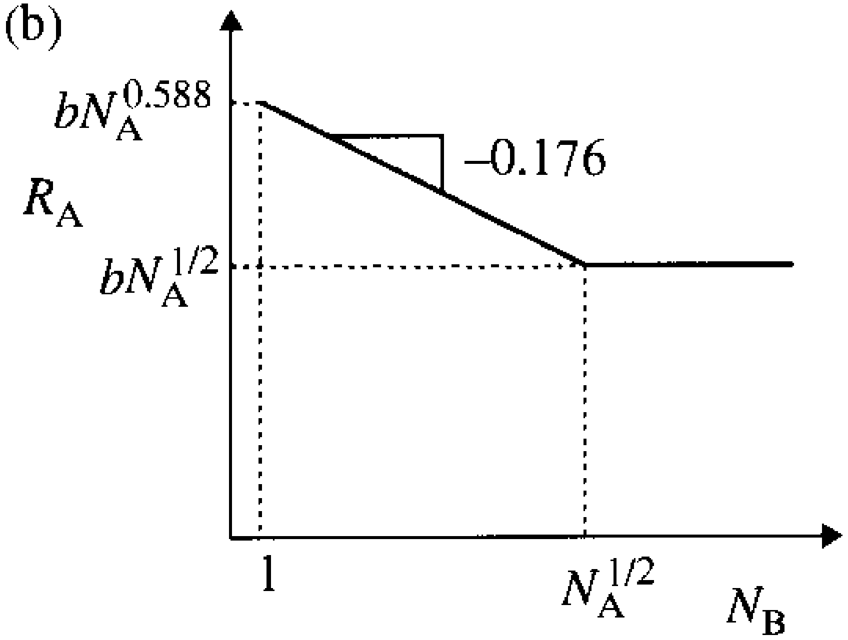
$$\xi_T \approx l g_T^{1/2} \approx l N_B$$

Polymer Chain in Melts

串滴并非像亚浓溶液那样处于随机高斯分布，而是由于短B链(溶剂)的存在具有体积排斥效应

$$g_T \approx N_B^2 \qquad \xi_T \approx lN_B$$

$$R_A \approx \xi_T\left(\frac{N_A}{g_T}\right)^{\nu} = lN_B\left(\frac{N_A}{N_B^2}\right)^{\nu} = lN_A^{1/2}\left(\frac{N_A}{N_B^2}\right)^{\nu-1/2} \qquad \nu = \frac{3}{5}$$



Overlap parameter *P*

3D $$P = \frac{R_A^3}{Nl^3} = \frac{N^{3/2}l^3}{Nl^3} = \sqrt{N}$$

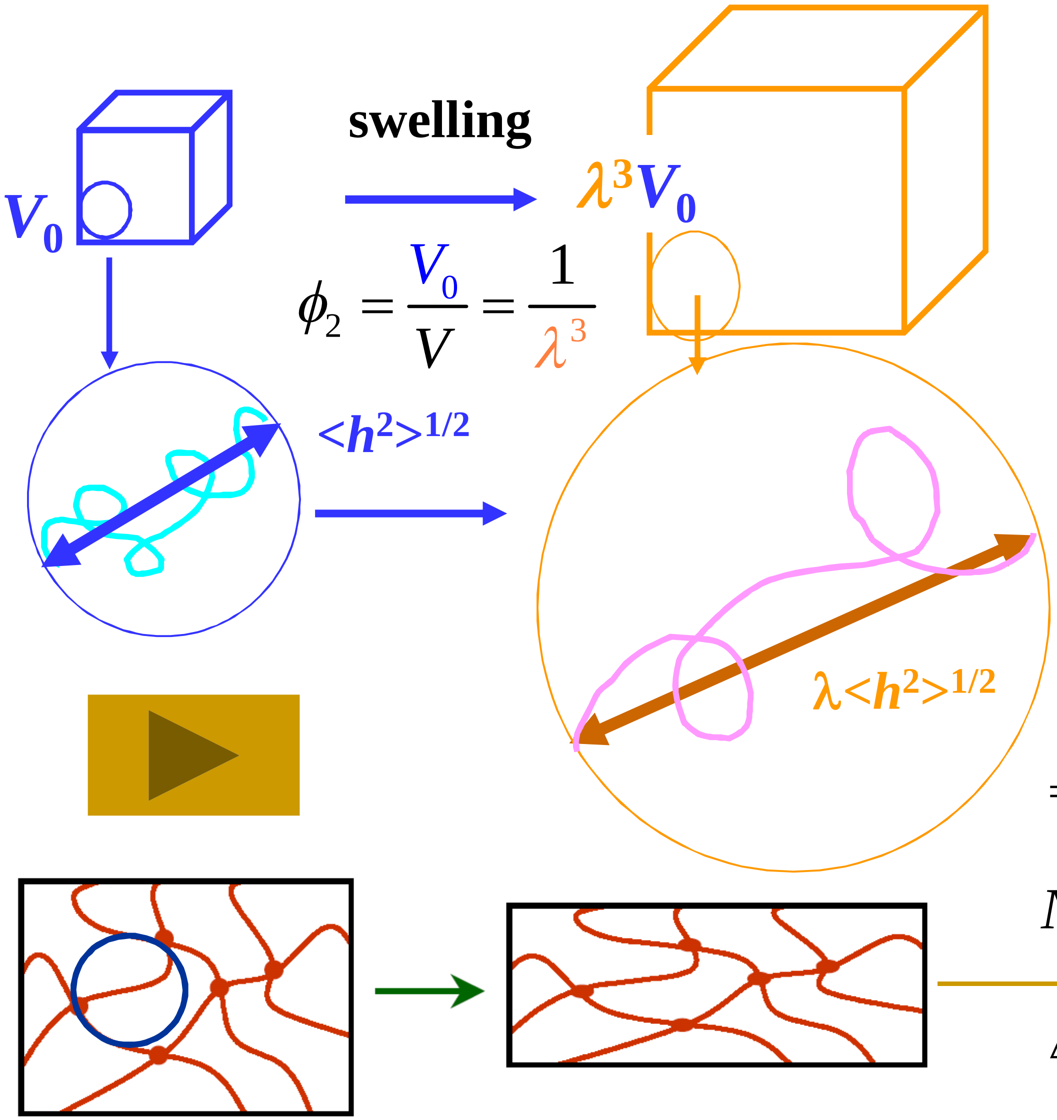
链与链之间发生强烈交叠

2D $$P \approx \frac{R^2}{Nl^2} = \frac{Nl^2}{Nl^2} = 1$$

两维链之间没有交叠

Flory猜测的熔体中链呈排斥体积被屏蔽的无扰状态完全正确！

3.7 Flory-Huggins free energy of a gel



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

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

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

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

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

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

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

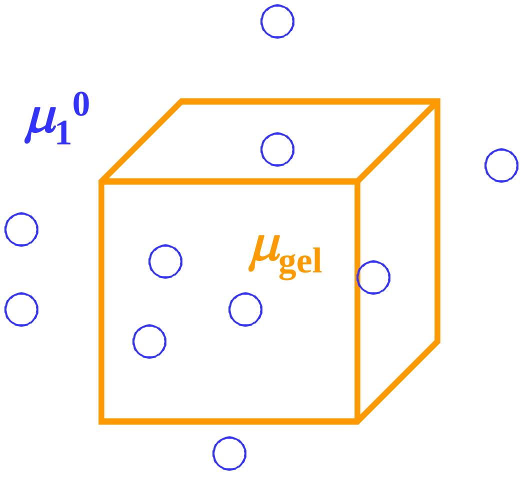
$$\overline{x}^2 = \overline{y}^2 = \overline{z}^2 = \frac{1}{3}h_0^2$$

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

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

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

Basic Equation of Gel Swelling



$$\mu_{gel}=\mu_1{}^0 \qquad \Delta\mu_1=\mu_{gel}-\mu_1{}^0=0$$

$$\Delta\mu_{gel}=\frac{\partial\Delta F}{\partial n_1}=\frac{\partial\Delta F_m}{\partial n_1}+\frac{\partial\Delta F_{elastic}}{\partial\phi_2}\frac{\partial\phi_2}{\partial n_1}=0$$

$$\frac{\partial\Delta F_m}{\partial n_1}=RT\left[\ln\left(1-\phi_2\right)+\left(1-\frac{1}{x}\right)\phi_2+\chi\phi_2^2\right]$$

$$=RT\left(\chi-\frac{1}{2}\right)\phi_2^2$$

$$\frac{\partial\Delta F_{elastic}}{\partial\phi_2}=-\frac{\rho_2 V_0}{\bar{M}_c}RT\phi_2^{-5/3}$$

$$\frac{\partial\Delta F_{elastic}}{\partial\phi_2}\frac{\partial\phi_2}{\partial n_1}=\frac{\rho_2\bar{V}_s}{\bar{M}_c}RT\phi_2^{1/3}$$

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

$$\Delta\mu_1/RT\doteq\left(\chi-\frac{1}{2}\right)\phi_2^2+\frac{\rho_2\bar{V}_1}{\bar{M}_c}\phi_2^{1/3}=0$$

$$\frac{\partial\phi_2}{\partial n_1}=\frac{\partial\left(\frac{V_0}{V_0+n_1\bar{V}_s}\right)}{\partial n_1}=-\frac{V_0}{\left(V_0+n_1\bar{V}_1\right)^2}\bar{V}_s=-\phi_2^2\frac{\bar{V}_s}{V_0}$$

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

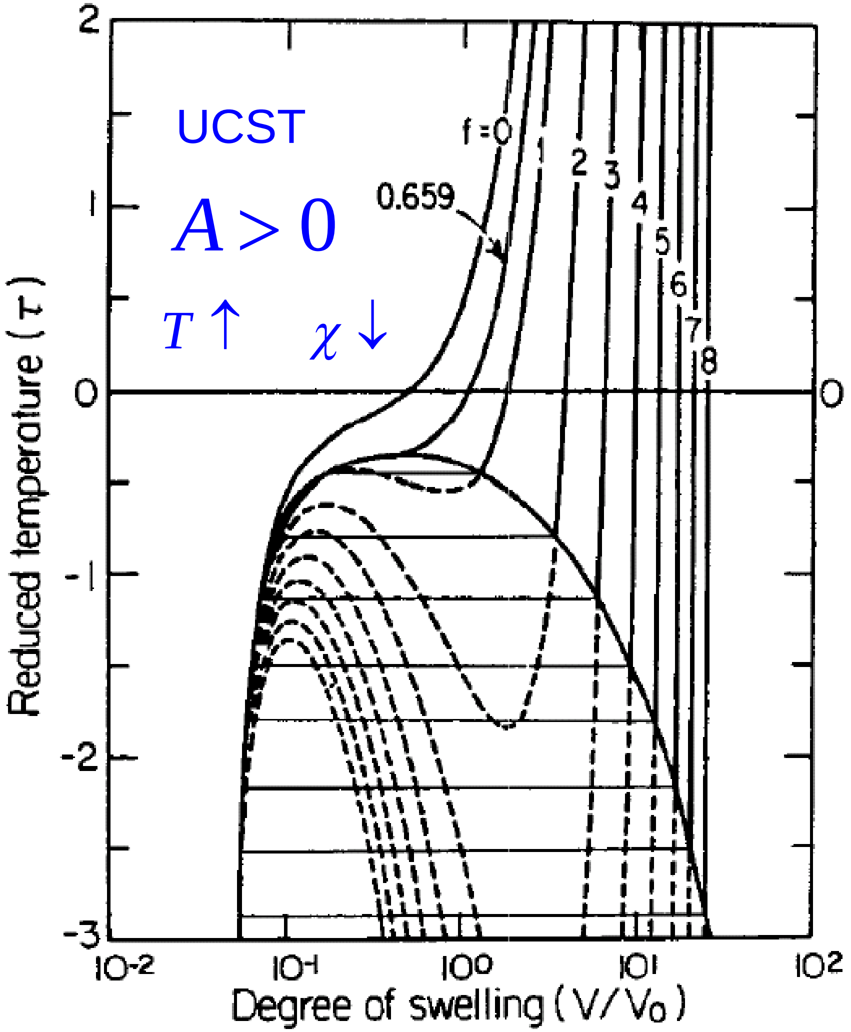
(1) 求χ

(2) 求M

$$Q=V/V_0=1/\phi_2=\lambda^3$$

$$Q\approx\bar{M}_c{}^{3/5}$$

Volume Phase Transition of Gels

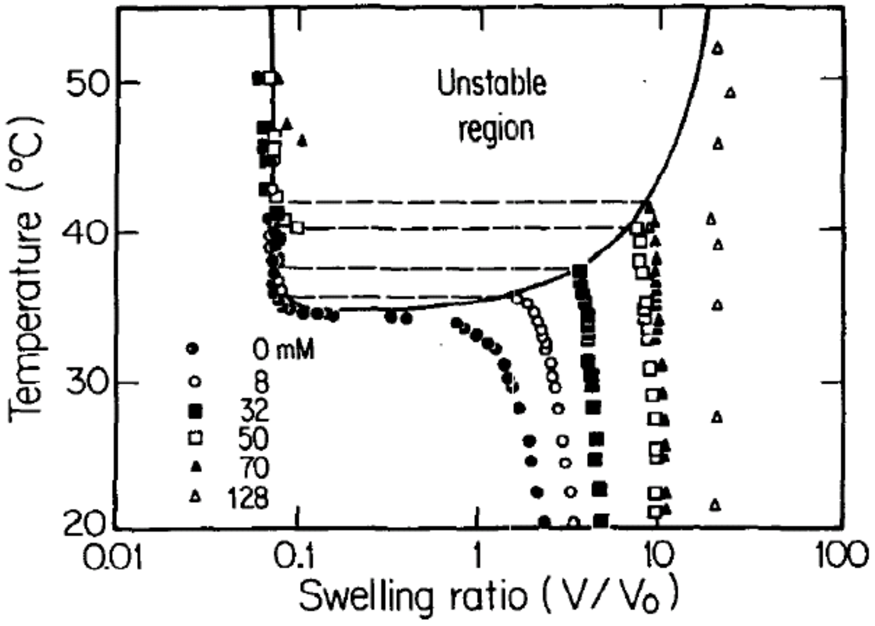


UCST

$A > 0$

$T\uparrow \quad \chi\downarrow$

$T\uparrow \quad \chi\uparrow$



Experiment

LCST $A < 0$

Theory, τ=1-2χ ~ 1-T_θ/T

Flory-Huggins Parameter

$$\chi = A / T + B$$

Problem: semi-dilute solution???

$$\Delta\mu_{gel} = \frac{\partial \Delta F}{\partial n_1} = \Delta\mu_1 + \frac{\partial \Delta F_{elastic}}{\partial \phi_2}\frac{\partial \phi_2}{\partial n_1} = 0$$

$$\Delta\mu_1 = \frac{\partial \Delta F_m}{\partial n_1} = RT\left[\ln(1-\phi_2) + \left(1-\frac{1}{x}\right)\phi_2 + \chi\phi_2^2\right]$$

$$= -\bar{V}_s\Pi \approx RT\left(\chi - \frac{1}{2}\right)\phi_2^2$$

$$\left\langle R_0^2 \right\rangle \approx N l^2$$

$$\Delta F_{elastic} \approx N k_B T \frac{\lambda^2 R_0^2}{R_{fluct}^2} = \frac{\rho_2}{\bar{M}_c} V_0 \tilde{N} k_B T \frac{\lambda^2 R_0^2}{R_{fluct}^2}$$

$$\bar{V}_s \boxed{\Pi} = \frac{\rho_2}{\bar{M}_c} V_0 RT \frac{\partial\left(\frac{\lambda^2 R_0^2}{R_{fluct}^2}\right)}{\partial \phi_2}\frac{\partial \phi_2}{\partial n_1} = -\frac{\rho_2}{\bar{M}_c}\bar{V}_s RT \boxed{\frac{\partial\left(\frac{\lambda^2 R_0^2}{R_{fluct}^2}\right)}{\partial \phi_2}}\phi_2^2$$

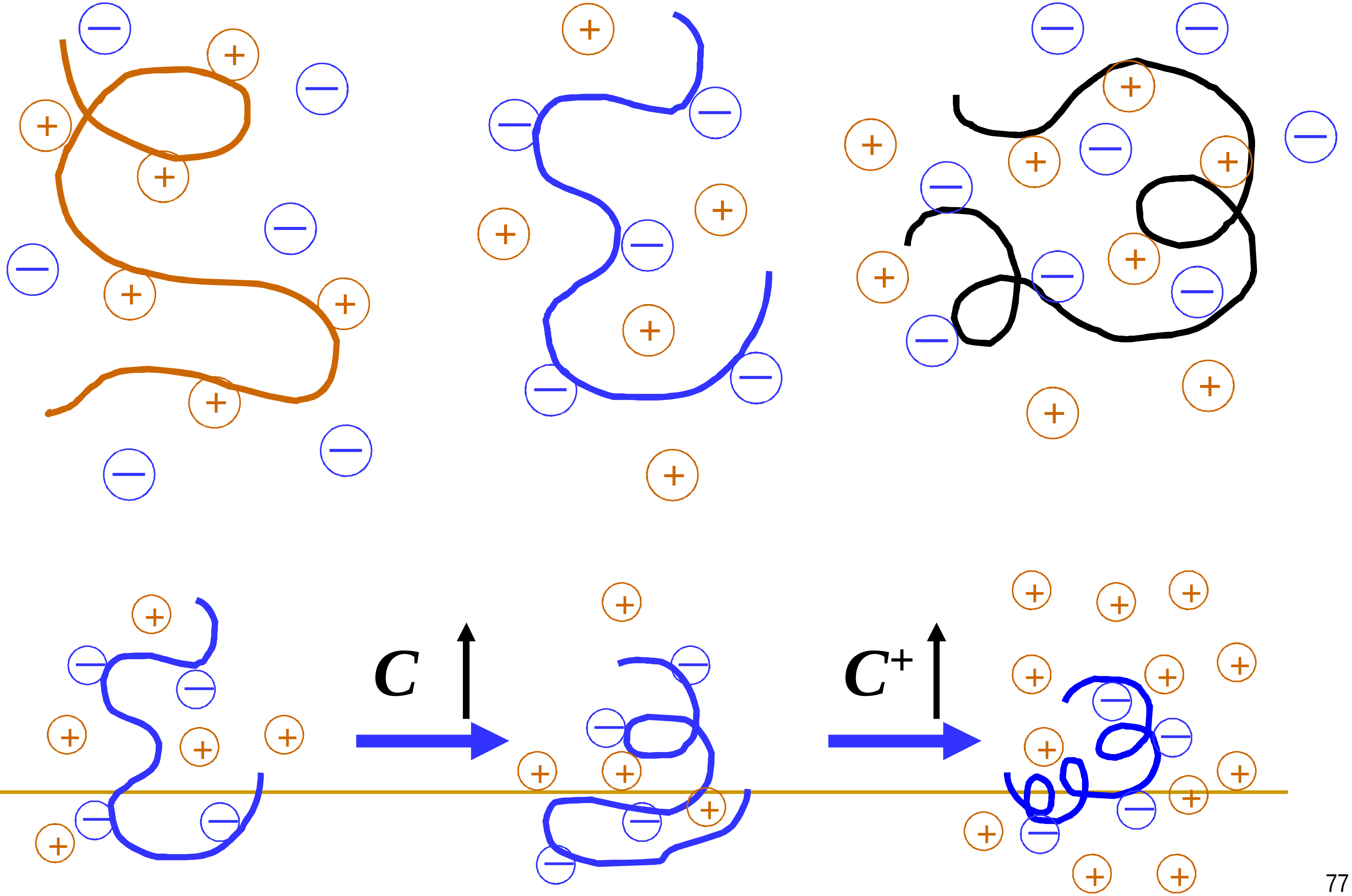
$$\frac{\partial \phi_2}{\partial n_1} = -\phi_2^2 \frac{\bar{V}_s}{V_0}$$

$$\Pi \propto c^{9/4}\tau^{?}$$

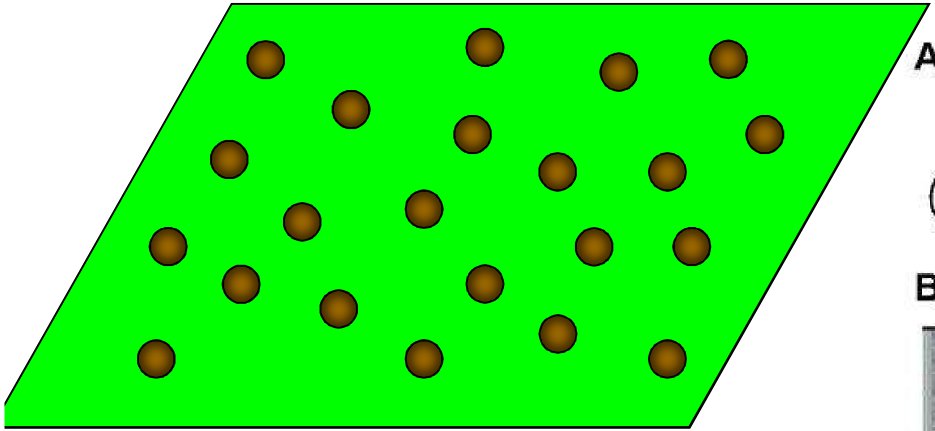
$$Q = \frac{V}{V_0} = \phi_2^{-1} = \lambda^3 \qquad \lambda = \phi_2^{-1/3}$$

$$\left\langle R_{fluct}^2 \right\rangle \approx N \phi_2^{-1/4} \tau^{1/4} l^2$$

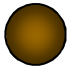
3.8 Solutions of Polyelectrolytes



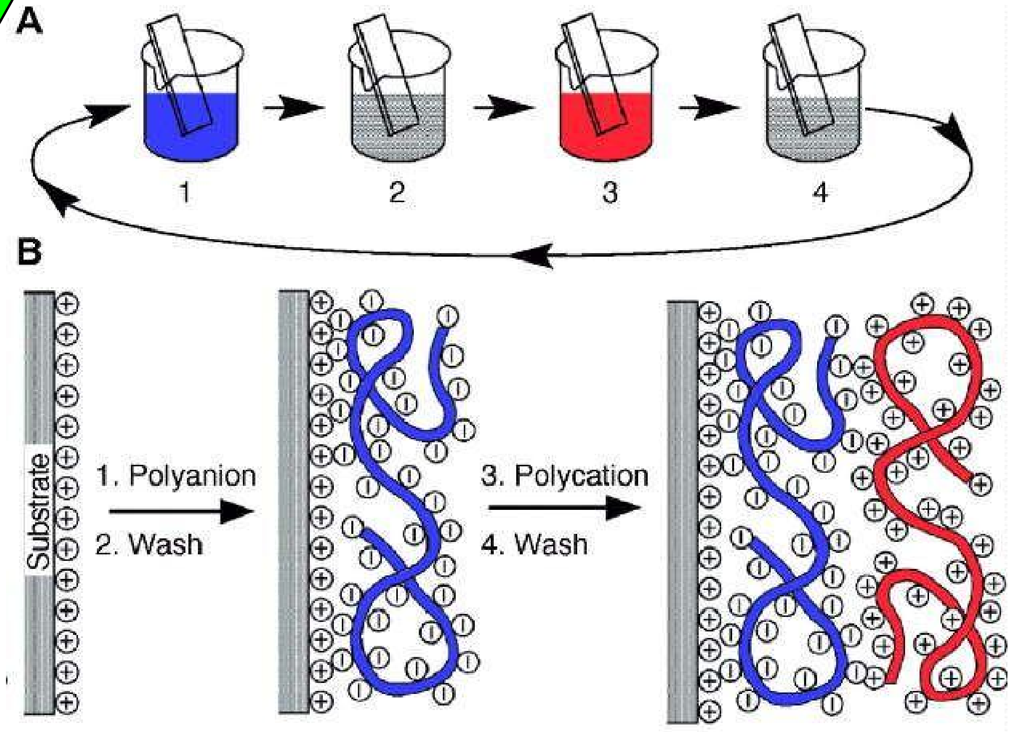
Charge Reversal & Layer by Layer Assembly



Oppositely charged plane



Polyion of charge Z



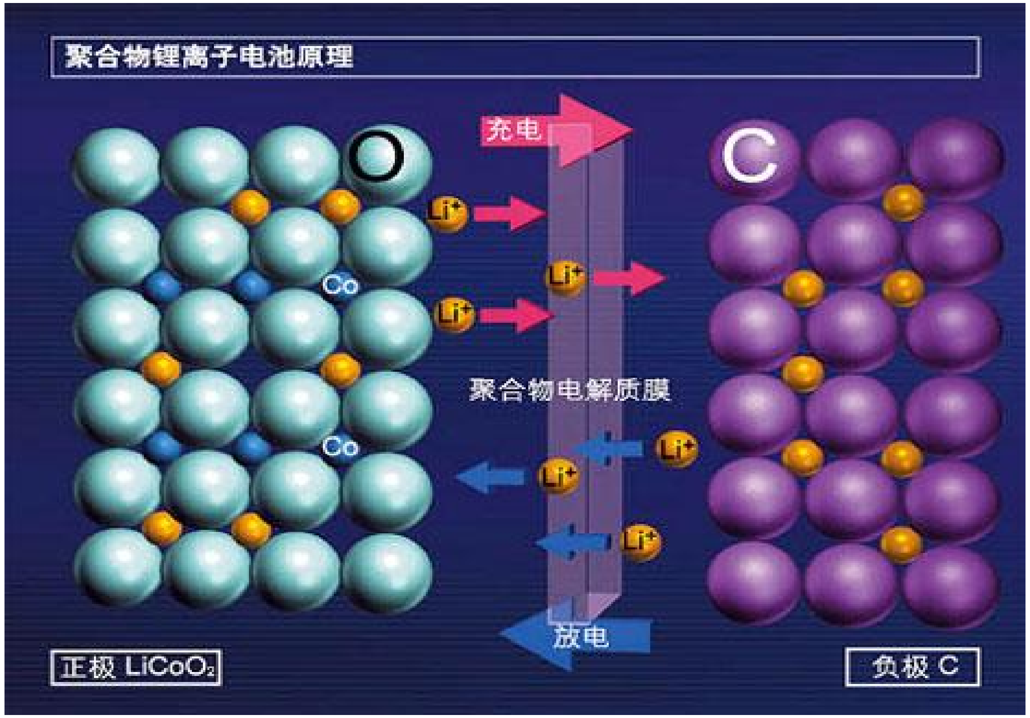
Li-ion Battery

Fits **NIKON** EN-EL2

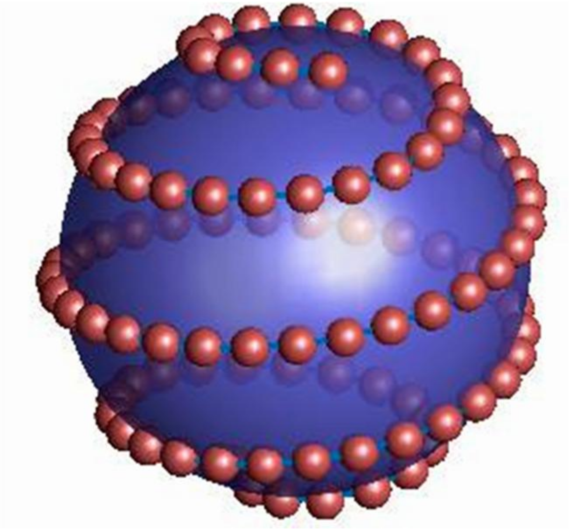
Li-ion 3.7V 1000mAh

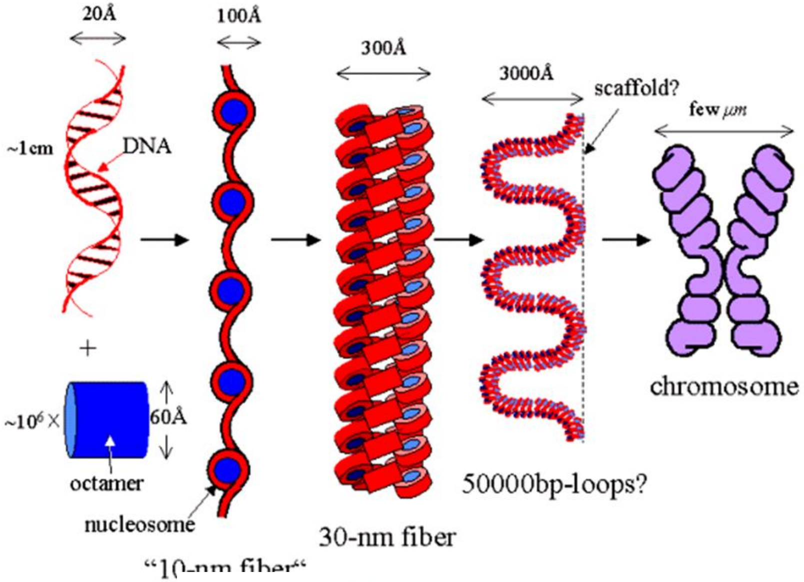
CAUTION

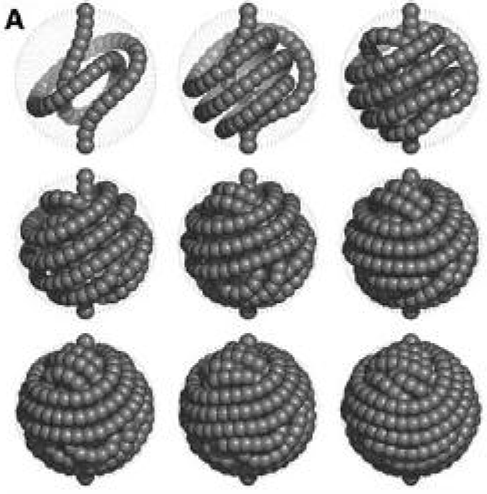
- DO NOT INCINERATE.
- DO NOT EXPOSE TO HIGH TEMPERATURES(140 F).
- DO NOT DISASSEMBLE.

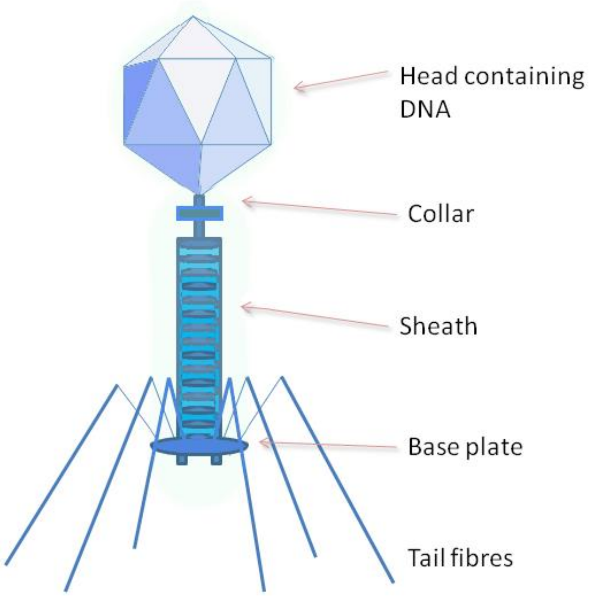


Wrapping a chain on/in a sphere





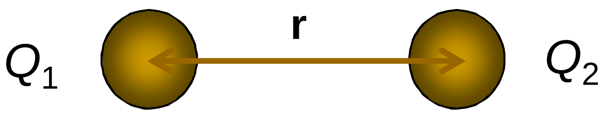




Appendix: Introduction to the theory of electrolytes

Long-range Coulomb interaction

- The **force** between two spherically symmetric charges in vacuum



$$f(\mathbf{r}) = \frac{Q_1 Q_2 e^2 \mathbf{r}}{4\pi\varepsilon_0 r^3}$$

- The **interaction energy** (in unit of k_BT) between two spherically symmetric charges in vacuum

$$U(r)/k_BT = \frac{Q_1 Q_2 e^2}{4\pi\varepsilon_0 r}$$

Compared to van der Waals Interaction

$$U_{LJ}/kBT = \frac{A}{r^{12}} - \frac{B}{r^6}$$

Summation of two-body Interactions within a Chain or a Blob

$$\bar{E}/k_BT = \frac{v_c}{2}\frac{N^2}{R^3}(1-2\chi)$$

Linearized Poisson-Boltzmann Equation - Debye-Hückel Theory

- When the electric potential is low ($|\phi|$<**25**mV), we can make the expansion and only keep the linear term. Thus the Debye-Hückel equation (linearlized Poisson-Boltzmann equation) is obtained. The Debye-Hückel treatment gives a simple (mean-field) description to the many-body interactions between ions.

$$\nabla^2\phi(\mathbf{r})=\frac{8\pi e^2 n_0}{\varepsilon}\left[\frac{\phi(\mathbf{r})}{k_BT}+\frac{1}{3!}e^2\left(\frac{\phi(\mathbf{r})}{k_BT}\right)^3+\ldots\right]\approx\frac{8\pi e^2 n_0}{\varepsilon k_BT}\phi(\mathbf{r})=\frac{1}{\lambda_D^2}\phi(\mathbf{r})$$

$$\boxed{\nabla^2\phi(\mathbf{r})=\lambda_D^{-2}\phi(\mathbf{r})}$$

where $\lambda_D=\sqrt{\dfrac{\varepsilon k_BT}{8\pi e^2 n_0}}=\sqrt{\dfrac{1}{8\pi l_B n_0}}$ $\quad l_B=\dfrac{e^2}{\varepsilon k_BT}$

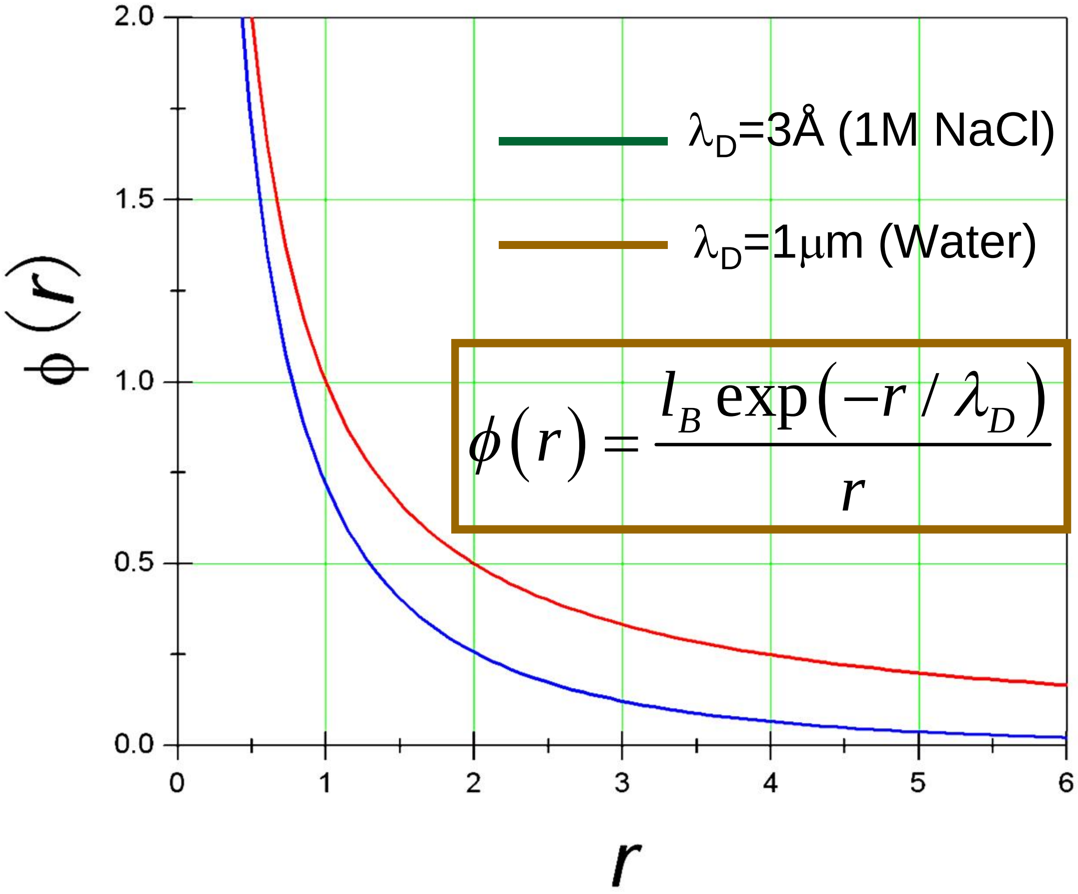
n_0 is the number density (per unit volume) of the ions.

l_B: Bjerrum长度

- In the limit of a strong electrolyte, the surface potential ϕ_S is small enough so a linearization of the P–B equation can be justified.

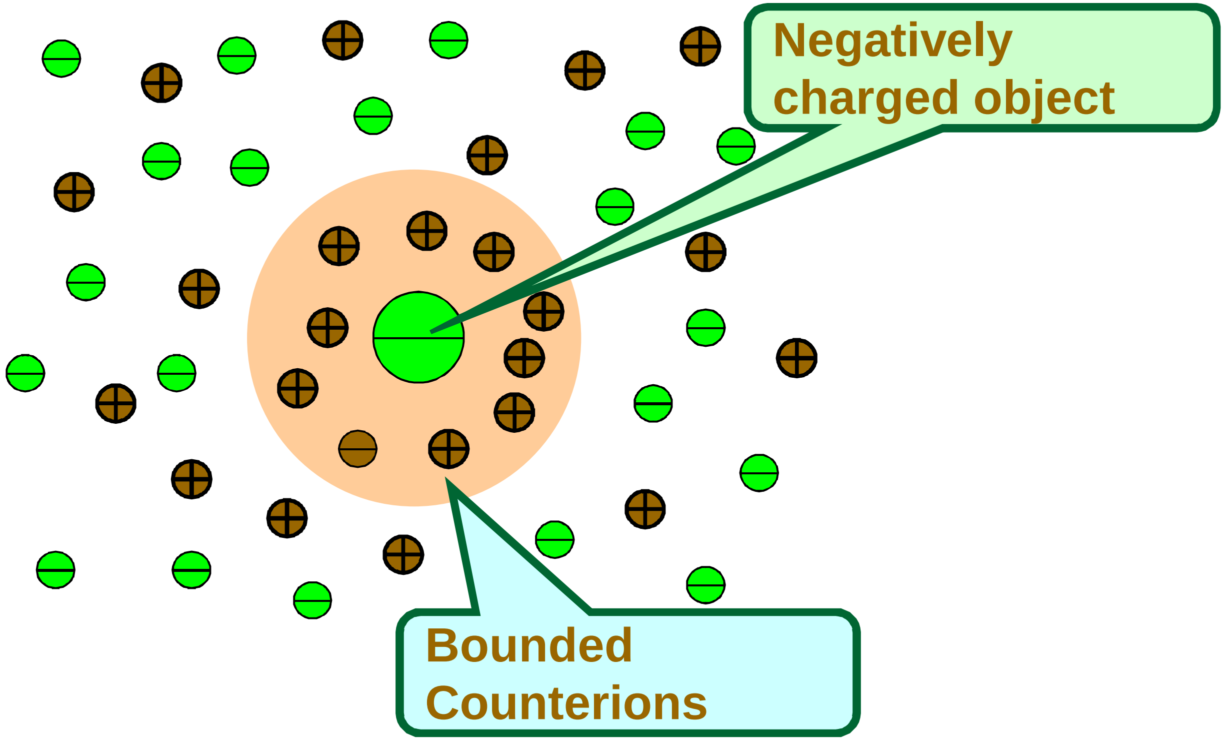
Debye-Hückel potential

- The effect of charge screening is dramatically different from the presence of a polarizable environment. As has been shown by Debye and Hückel 80 years ago, screening modifies the electrostatic interaction such that it falls off exponentially with distance.



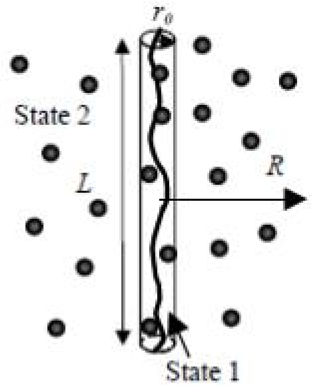
$$\phi(r) = \frac{l_B \exp\left(-r/\lambda_D\right)}{r}$$

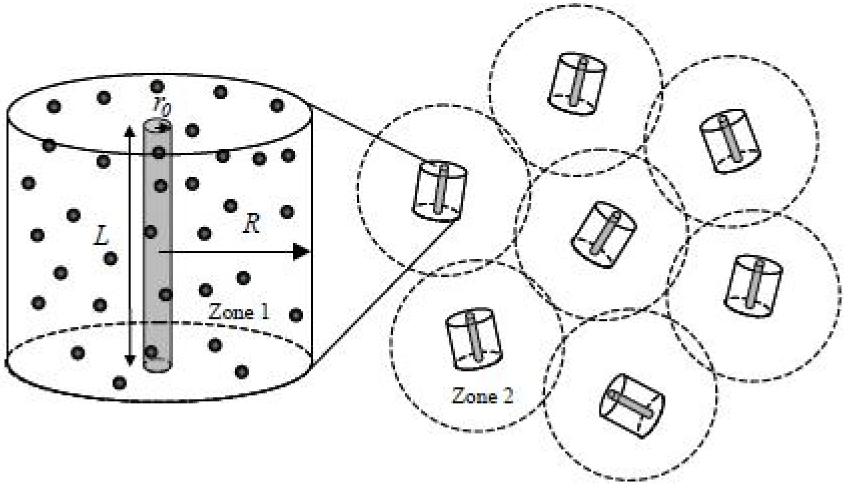
Charge screening

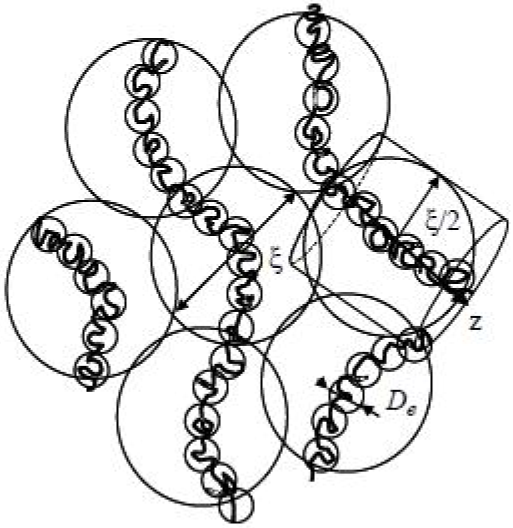


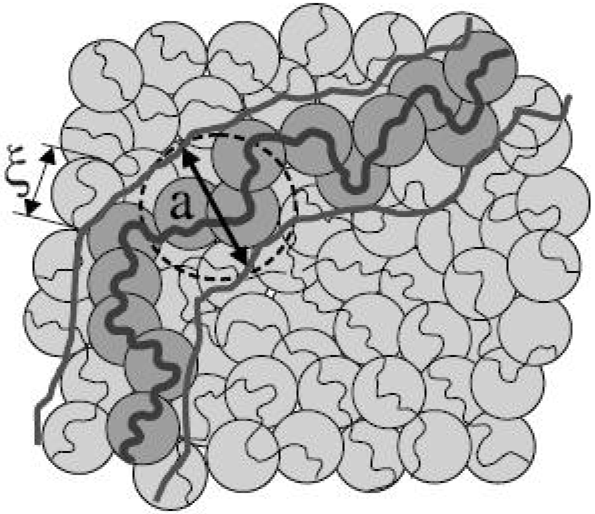
- Salt ions of opposite charge are drawn to charged objects and form loosely bound counter-ion clouds and thus effectively reduce their charges. This process is called screening.

Polyelectrolyte in solution









Semi-dilute

concentrated

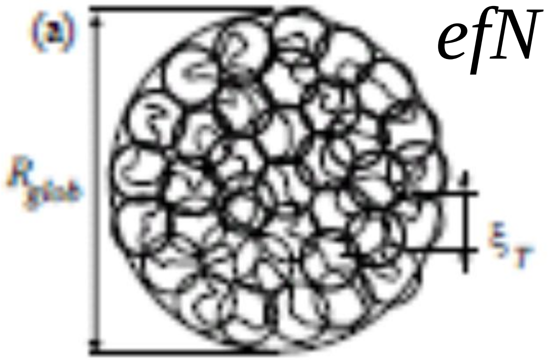
Theoretical Model of A Single Polyelectrolyte Chain

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

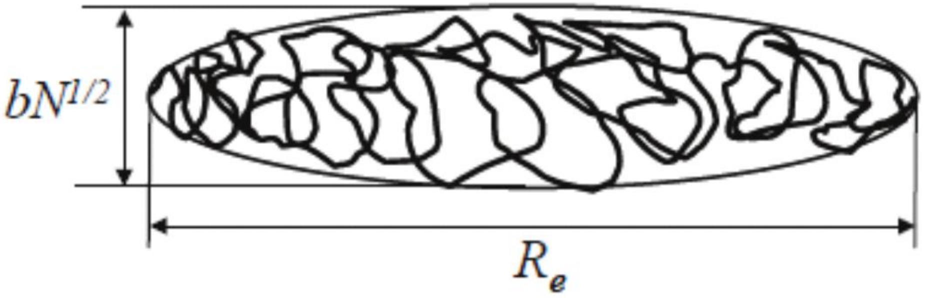
$$\frac{F_{\text{conf}}\left(R_e\right)}{k_B T}\approx\frac{R_e^2}{N l^2}$$

Guassian Chain

l: Kuhn segment



or



$$\frac{F_{electr}\left(R_e\right)}{kT}\approx\frac{l_{\mathrm{B}}\left(fN\right)^2}{R_e}$$

or

$$\frac{F_{electr}\left(R_e\right)}{kT}\approx\frac{l_{\mathrm{B}}\left(fN\right)^2}{R_e}\ln\left(\frac{R_e}{N^{1/2} l}\right)$$

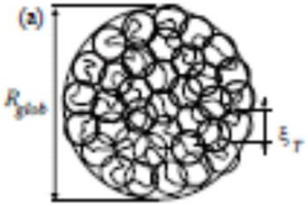
l_B**为Bjerrum**长度 $l_{\mathrm{B}}=e^2/\left(\varepsilon k_B T\right)$ $u_B=l_B/l$

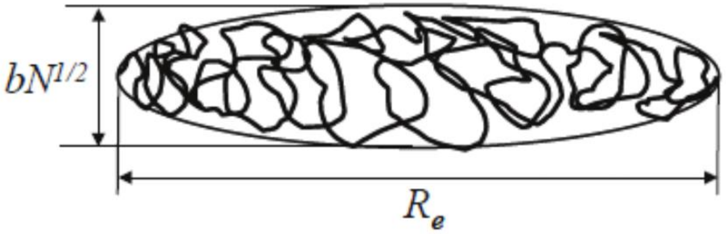
$$\frac{\partial F\left(R_e\right)}{\partial R_e}=0$$

(1) A Single Polyelectrolyte Chain in good solvents

Good solvent, $\chi<1/2$:

$$R_e \approx N l u_B^{1/3} f^{2/3} \qquad \text{or} \qquad R_e \approx N l u_B^{1/3} f^{2/3}\left[\ln\left(eN\left(u_B f^{2}\right)^{2/3}\right)\right]^{1/3}$$

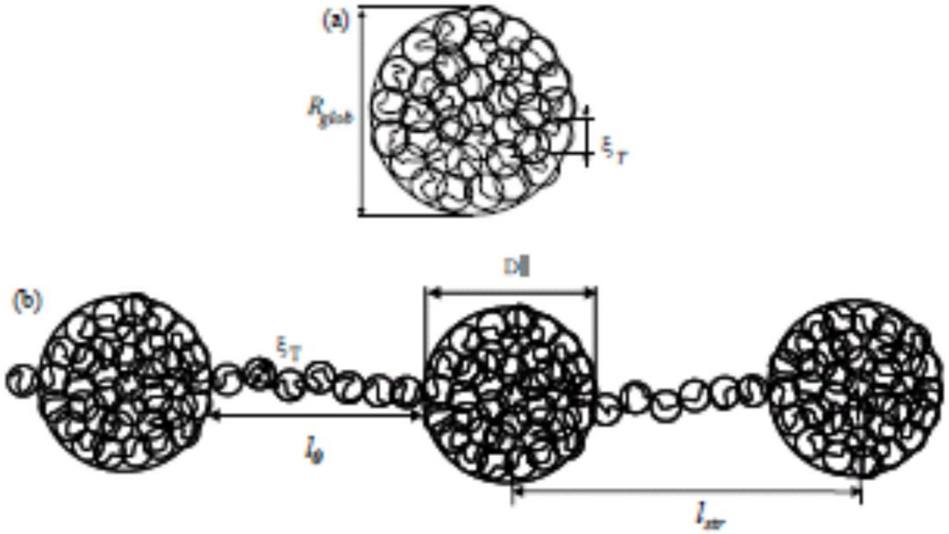




$$R_e >> N^{1/2}$$

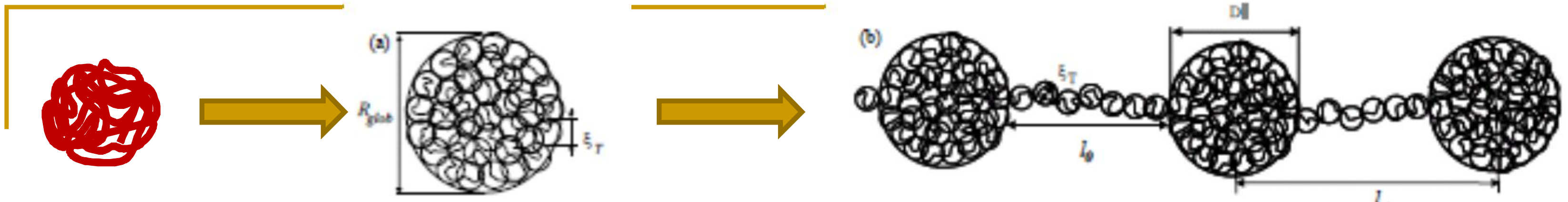
(2) A Single Polyelectrolyte in poor solvents

Poor solvent, $\chi>1/2$:



N is small

N is large

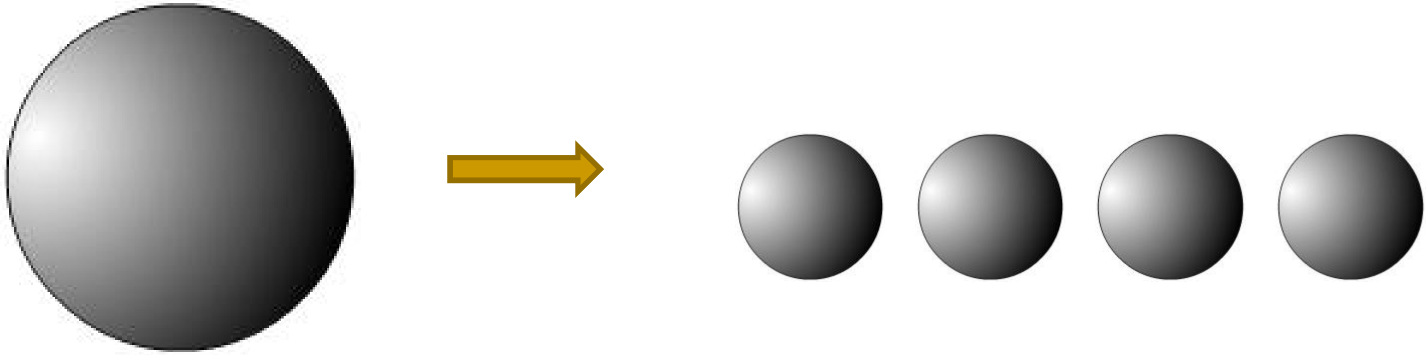


Blob

Bead (globule)

Beads+ Strings = necklace

Rayleigh instability of a charged droplet – 1882

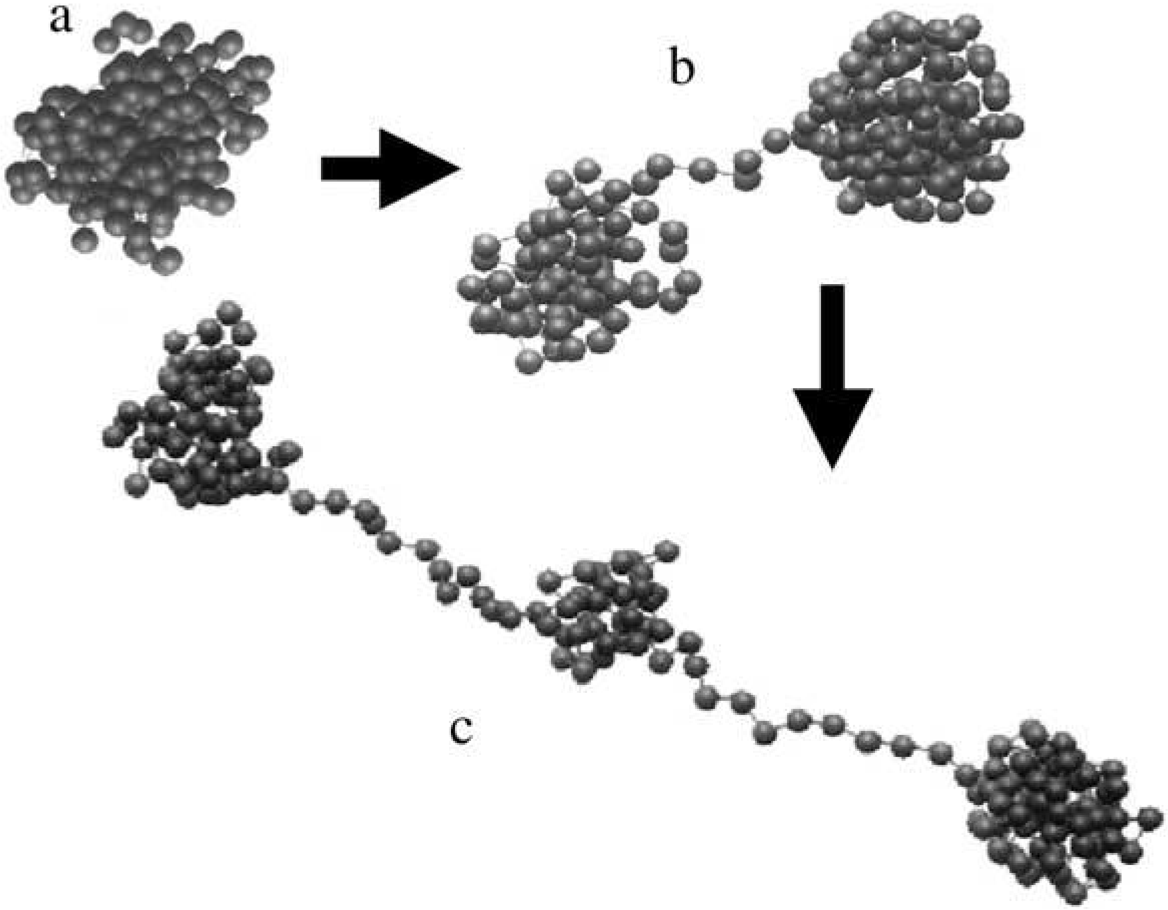


the break-up of a charged drop of liquid into droplets due to electrostatic repulsion

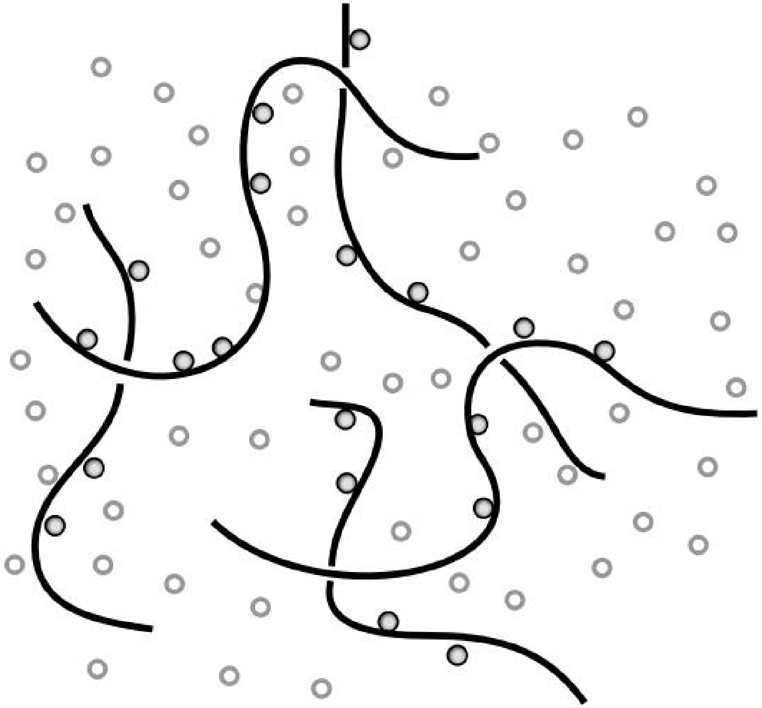
$$F_{Rayleigh}/k_BT = \frac{Q^2}{\varepsilon R_{drop}} + \gamma R_{drop}^2 \xrightarrow{\partial F_{Rayleigh}/\partial R_{drop} = 0} Q_{crit} \sim R_{drop}^{3/2}$$

$$\begin{aligned} F_{electro} &= k_BTl_B\left(fN\right)^2/R_{glob} \\ F_{surf} &= k_BTR_{glob}^2/\xi_T^2 \end{aligned} \xrightarrow[R_{glob} \approx l\left|\tau\right|^{-1/3}N^{1/3}]{\xi_T = l\left|\tau\right|^{-1}} f_{crit} \approx \left(\frac{\left|\tau\right|}{u_BN}\right)^{1/2}$$

Computer Simulations

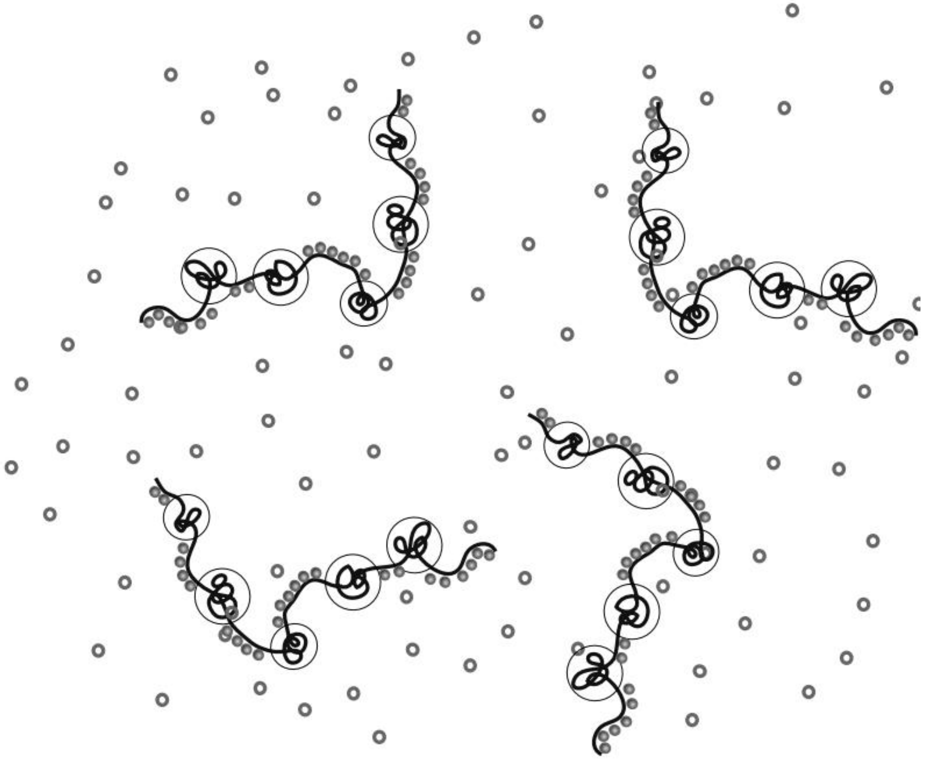


Topics not Discussed: Hydration and Associating in Polymer Solutions

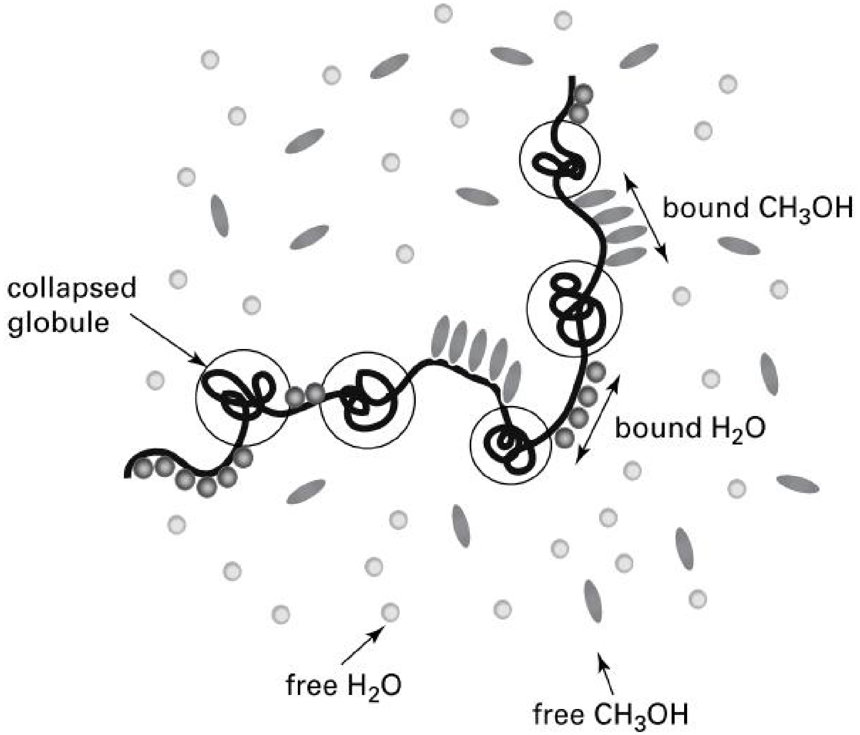


Hydration

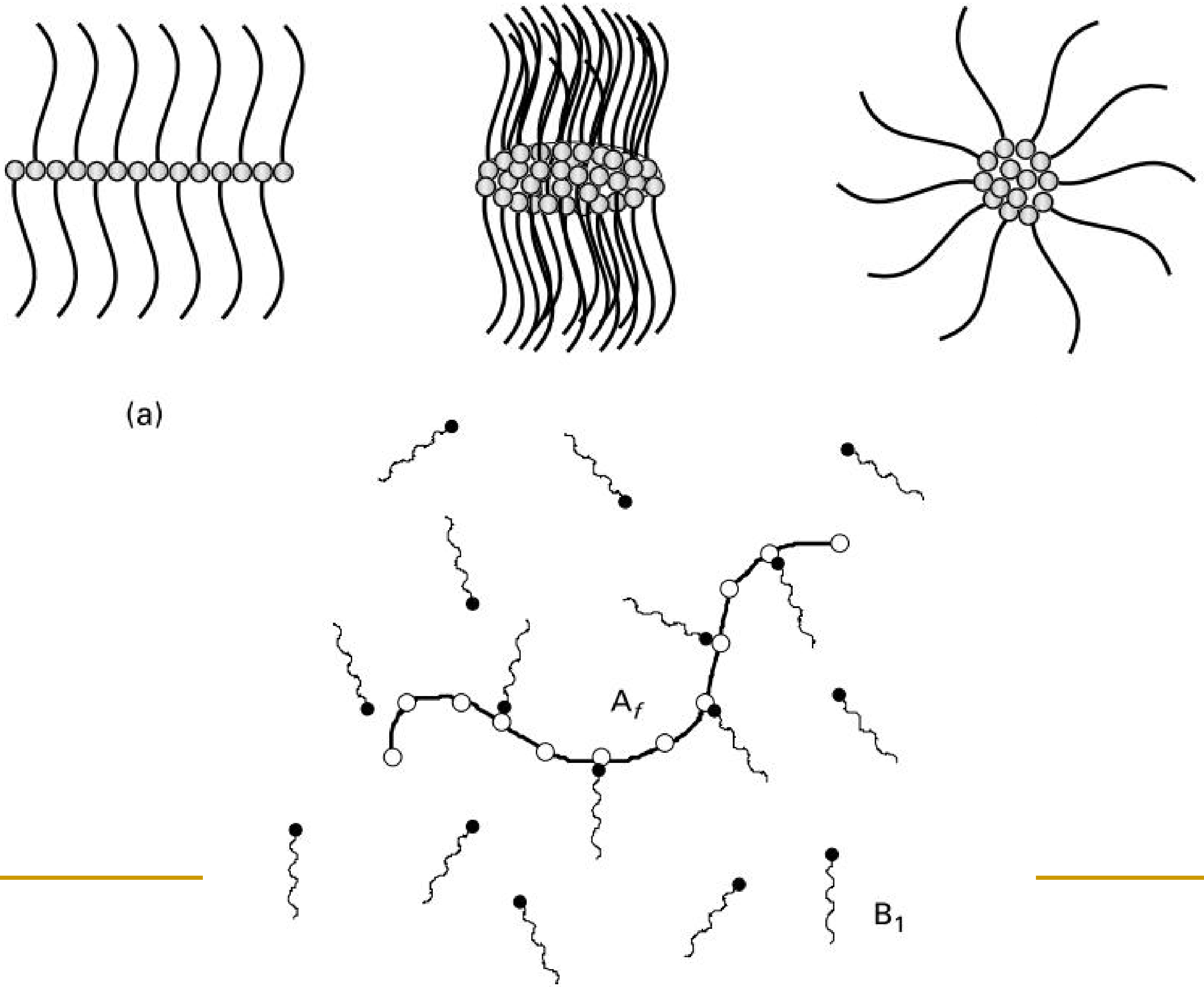
PNIPAM (*N* -异丙基丙烯酰胺) in Water



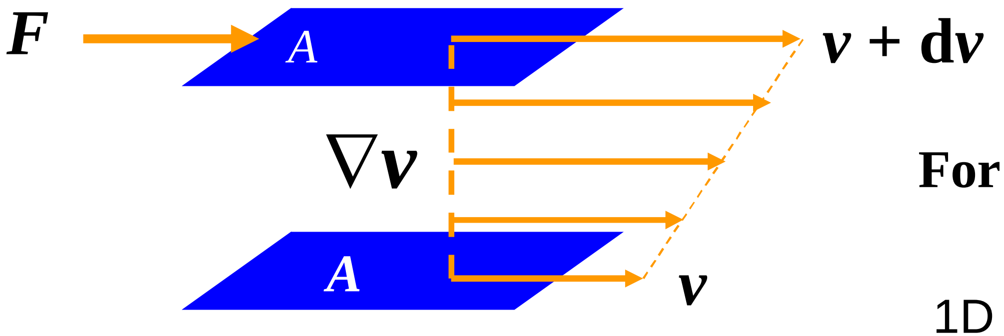
and Mixed Solvents



Topics not Discussed: Associating Polymer Solutions



3.9 Hydrodynamics Properties of Polymer Solutions



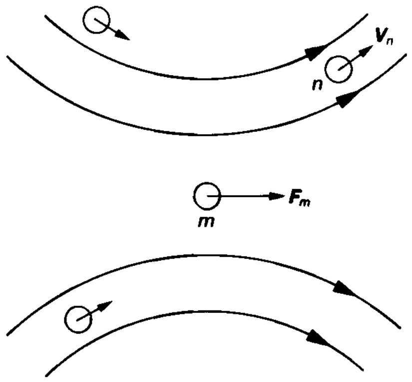
$$\boldsymbol{\sigma}=\boldsymbol{F}/A$$

For Newtonian fluids

1D $\boldsymbol{\sigma}=\eta\boldsymbol{v}$

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

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

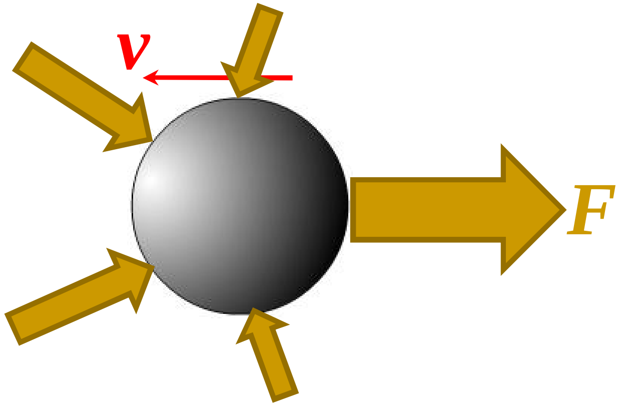


$$\boldsymbol{v}_{n}\left(\boldsymbol{r}\right)=\sum_{m}\boldsymbol{H}_{nm}\cdot\boldsymbol{F}_{m}$$

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

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

Diffusion of Suspensions in Solution



Stokes formula

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

Fick's law

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

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

Stokes-Einstein relation

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

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

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

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

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

hydrodynamics radius: R_h

Effective viscosity of suspensions

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

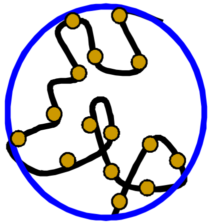
$$\eta = \eta_0 \left(1 + 2.5\Phi\right)$$

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)

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

N_A : Avogadro Number

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

V_h hydrodynamics volume

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

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

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

扩张因子

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

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

χ=1/2

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

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

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

For Θ solution

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

For flexible chain in good solvent

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

For stiff chain

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

For flexible chain ***a*=0.5~0.8**

For stiff chain ***a*=0.8~1.2**

Rouse-Zimm Model

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

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

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

$$\phi_{0(\mathrm{RZ})} = 0.425N_A = 2.56\times10^{23}$$

$$\phi_{0(\exp)} = 2.2 \sim 2.87\times10^{23}$$

Chapter 4 Multi-component Polymer Systems

- **4.1 Thermodynamics of Polymer Mixtures**
- **4.2 Properties of Polymer Interface**
- **4.3 Thermodynamics of Block Copolymers**

Mixing?

Polymer A

Polymer B

Polymer Blends

4.1 Thermodynamics of Polymer Mixtures

Why are two kinds of polymers not compatible?

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

Entropy of Mixing

N_1Polymer/N_2Polymer $$\Delta S^{p}_{xN_1,xN_2} = -k\left(N_1 \ln\frac{xN_1}{xN_1+xN_2} + N_2 \ln\frac{xN_2}{xN_1+xN_2}\right)$$

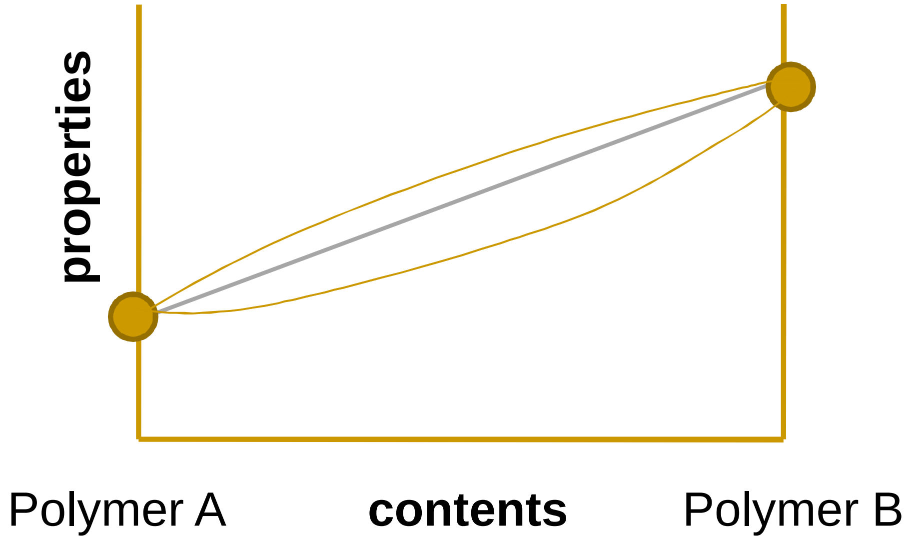
N_1Solvent/N_2Solvent $$\Delta S^{s}_{N_1,N_2} = -k\left(N_1 \ln\frac{N_1}{N_1+N_2} + N_2 \ln\frac{N_2}{N_1+N_2}\right)$$

xN_1Solvent/xN_2Solvent $$\Delta S^{s}_{xN_1,xN_2} = -k\left(xN_1 \ln\frac{xN_1}{xN_1+xN_2} + xN_2 \ln\frac{xN_2}{xN_1+xN_2}\right)$$

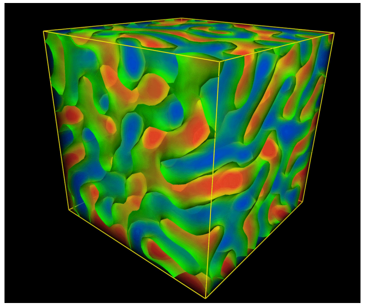
$$\left|\Delta S^{p}_{xN_1,xN_2}\right| \sim \left|\Delta S^{s}_{N_1,N_2}\right| << \left|\Delta S^{s}_{xN_1,xN_2}\right|$$

The importance of multi-component, multi-phase materials

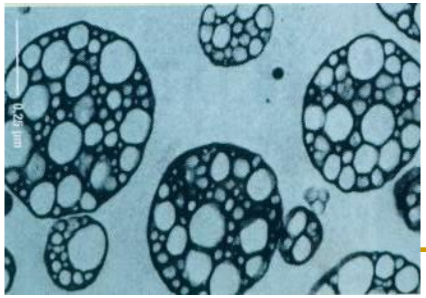
homogenous

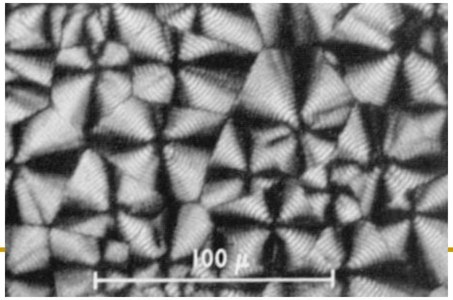


heterogeneous



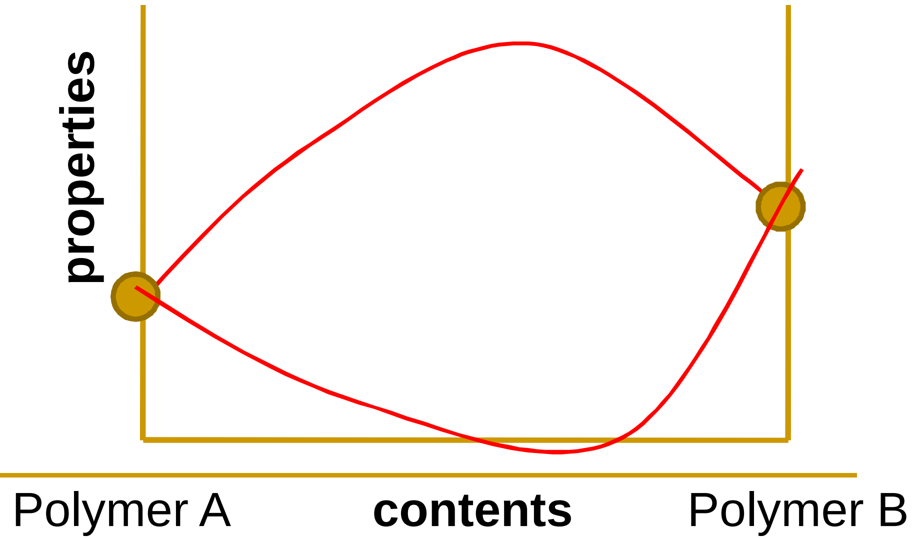
Polymer blends





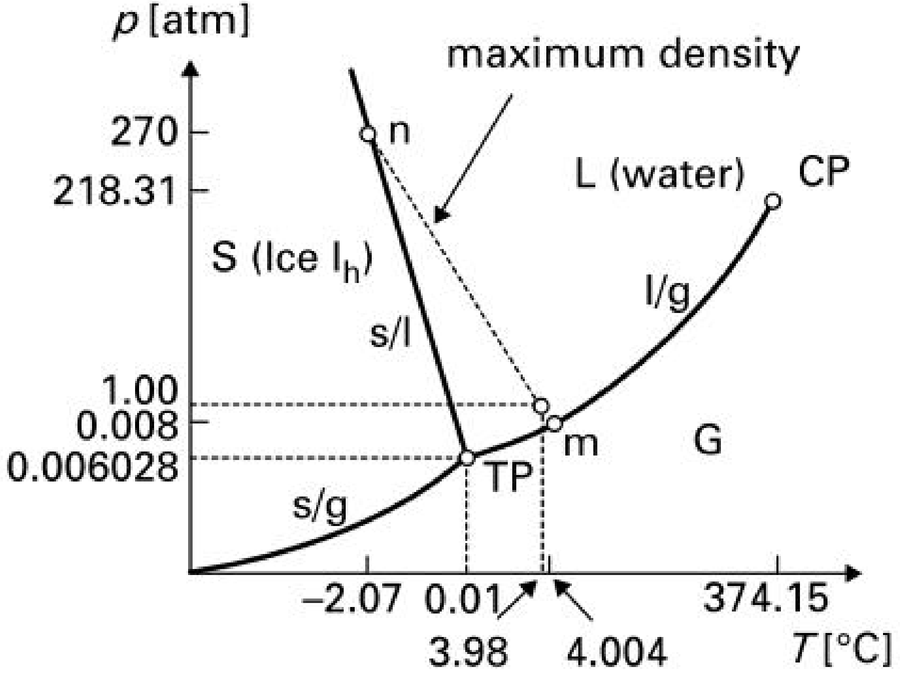
HIPS, ABS

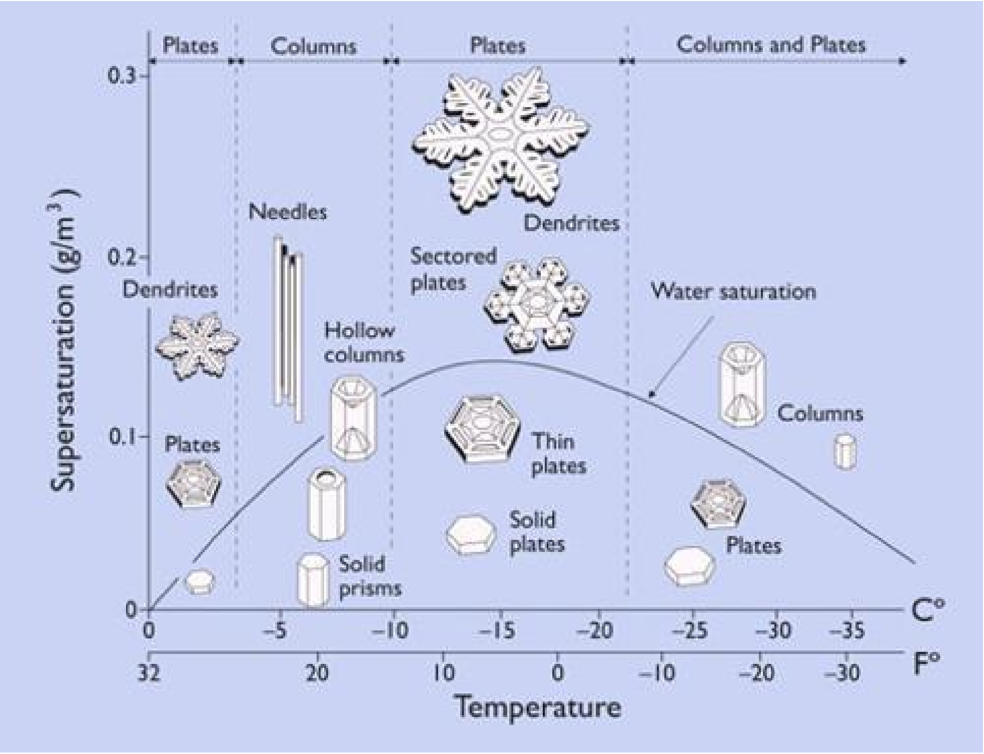
Polyolefins



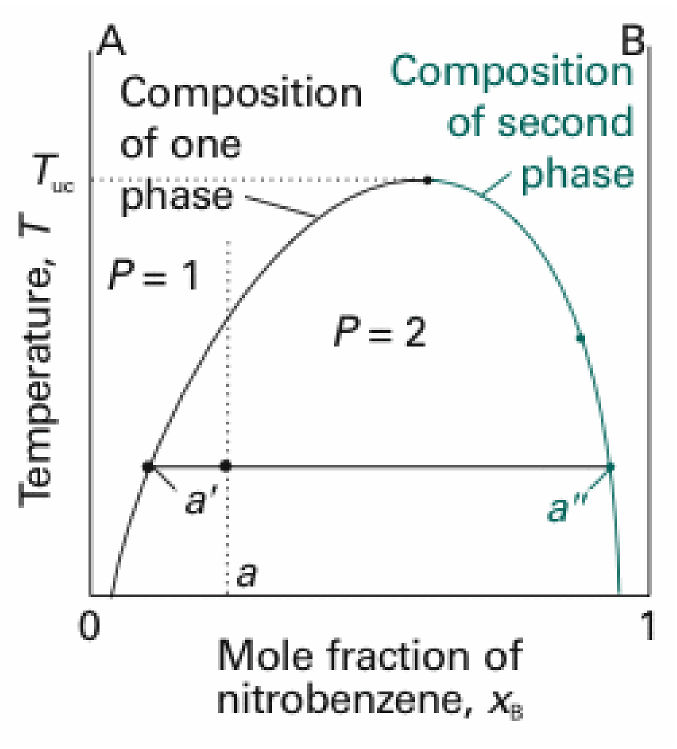
crystallinity

Typical Phase Diagram of One Component

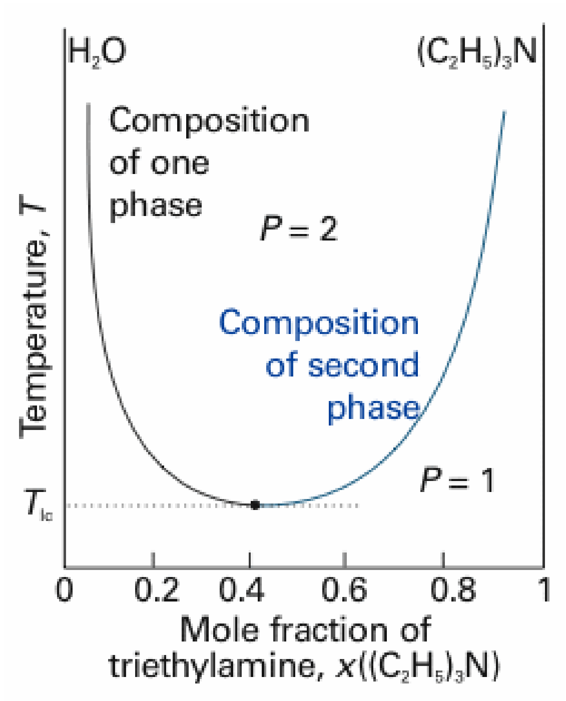




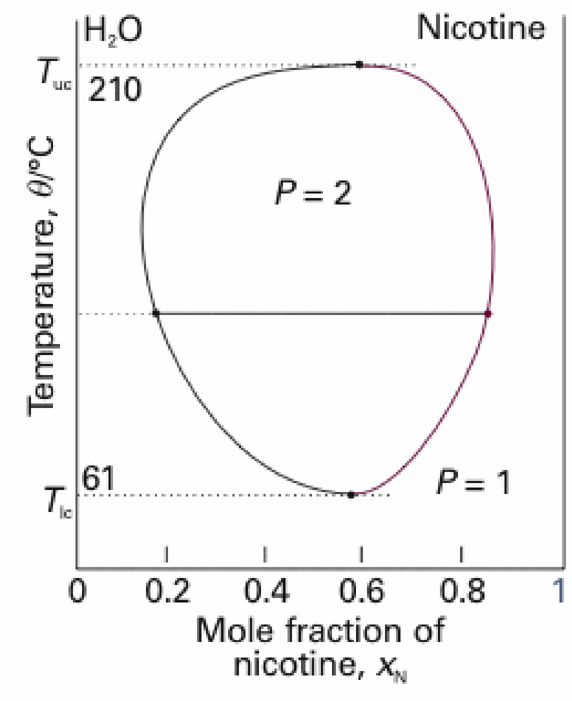
Typical Phase Diagram of Mixture I: Liquid-Liquid



UCST

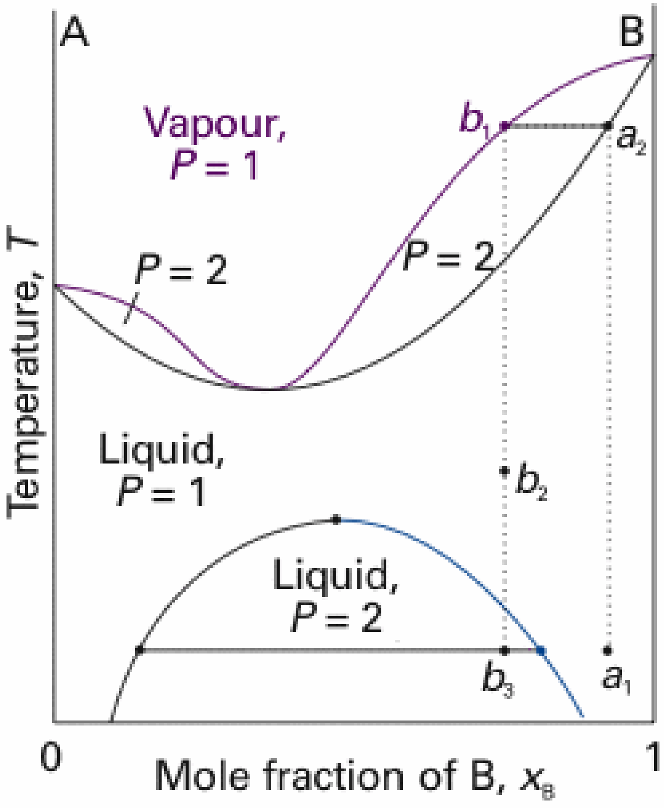


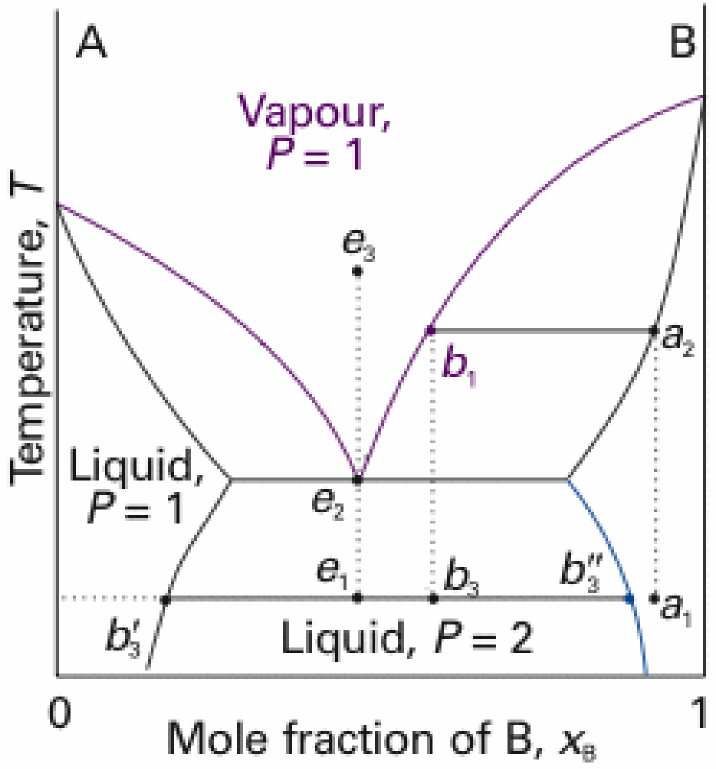
LCST



LCST + UCST

Typical Phase Diagram of Mixture II: Liquid-Liquid & Liquid-Vapour

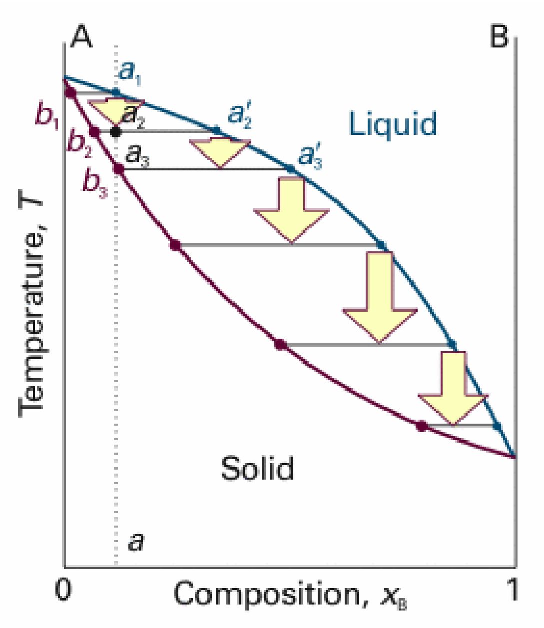


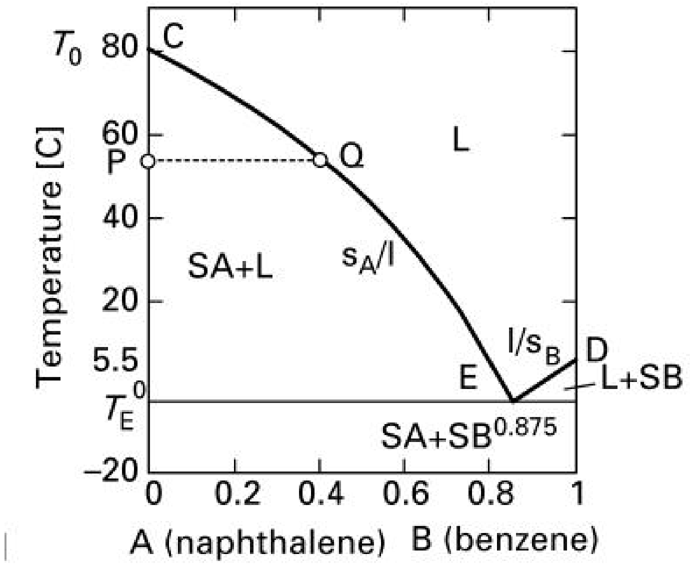


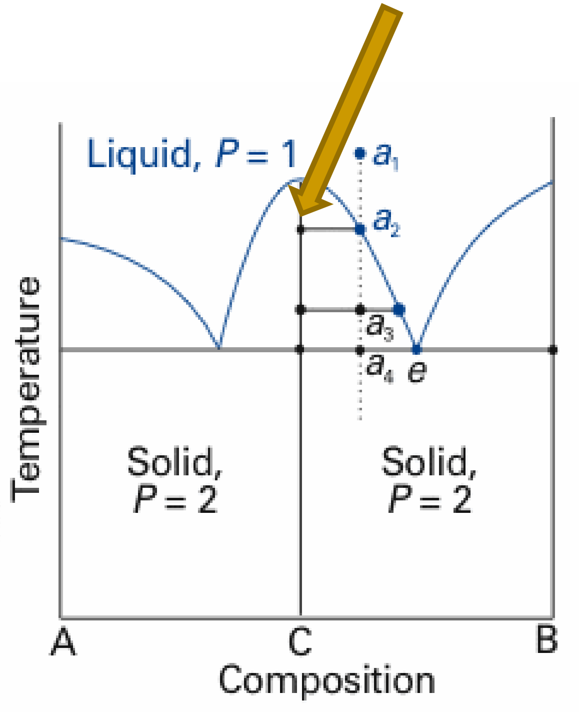
There is no Vapour Phase in Polymer System

Typical Phase Diagram of Mixture III: Liquid-Solid & Solid-Solid

& Liquid-Liquid

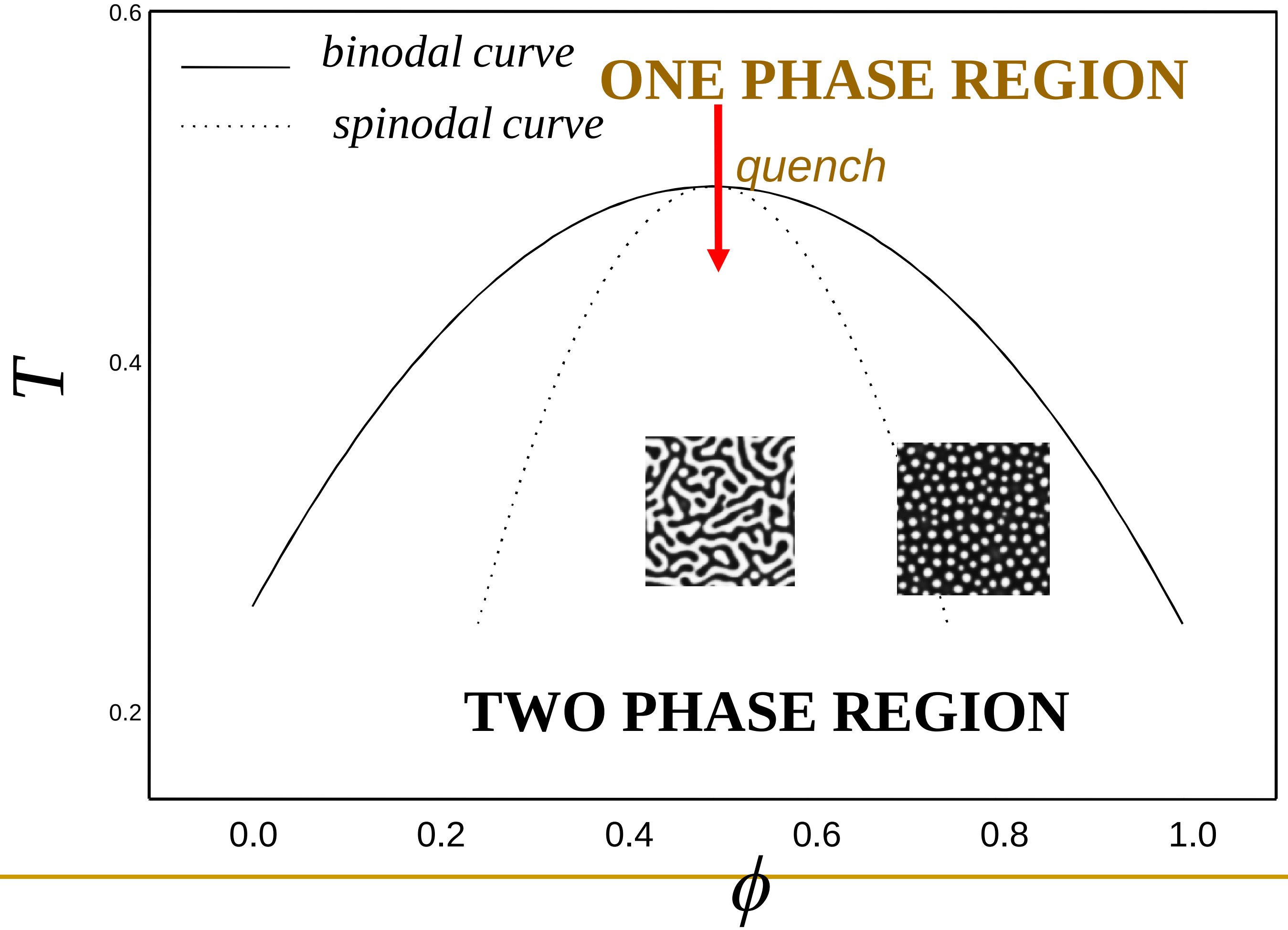




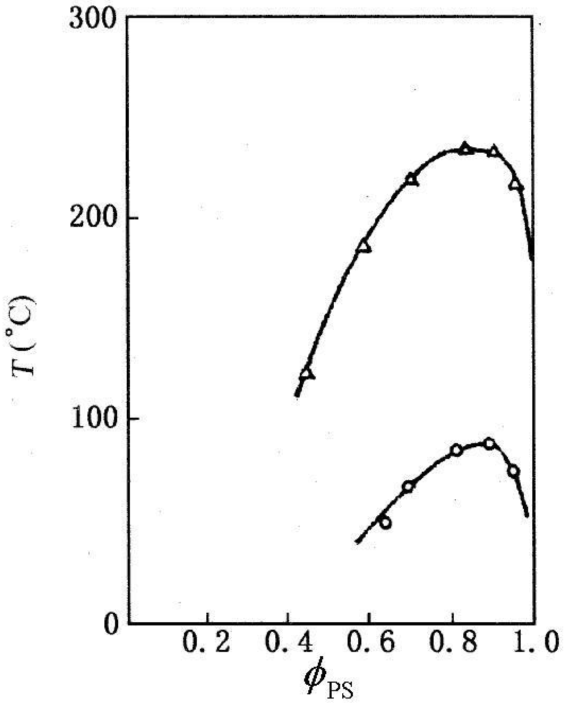


There may exit Solid Phase in Polymer System

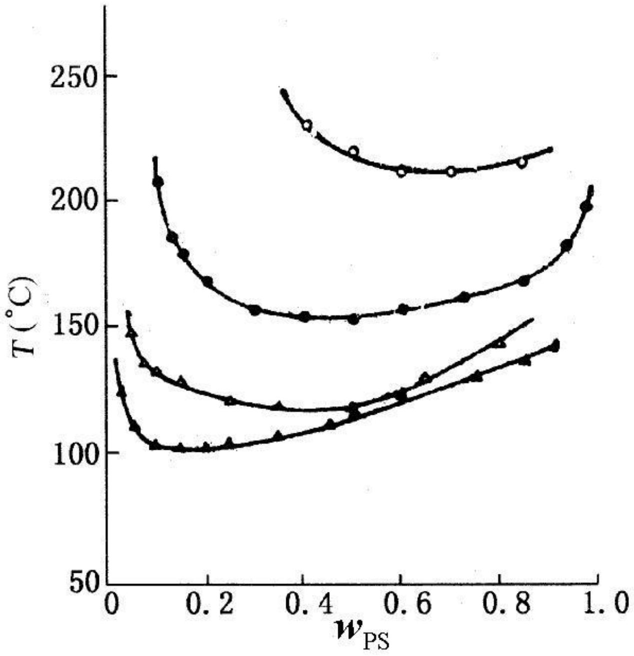
Relation between phase diagram and morphology



Phase Diagrams of Polymer Blends



UCST

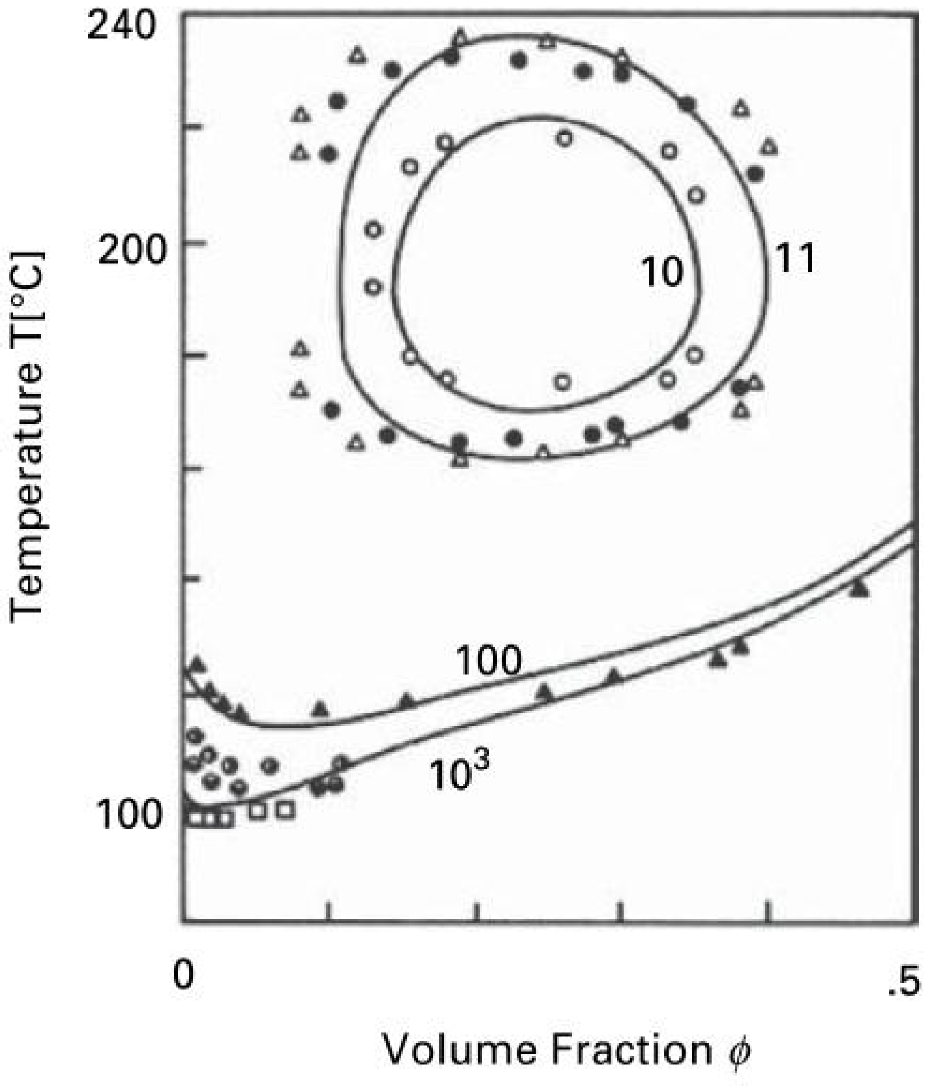


LCST

$$\chi = \frac{(Z-2)\Delta\varepsilon_{12}}{kT} = \frac{A}{T} \quad A > 0$$

$$A < 0???$$

Phase diagram of aqueous solutions of PEO

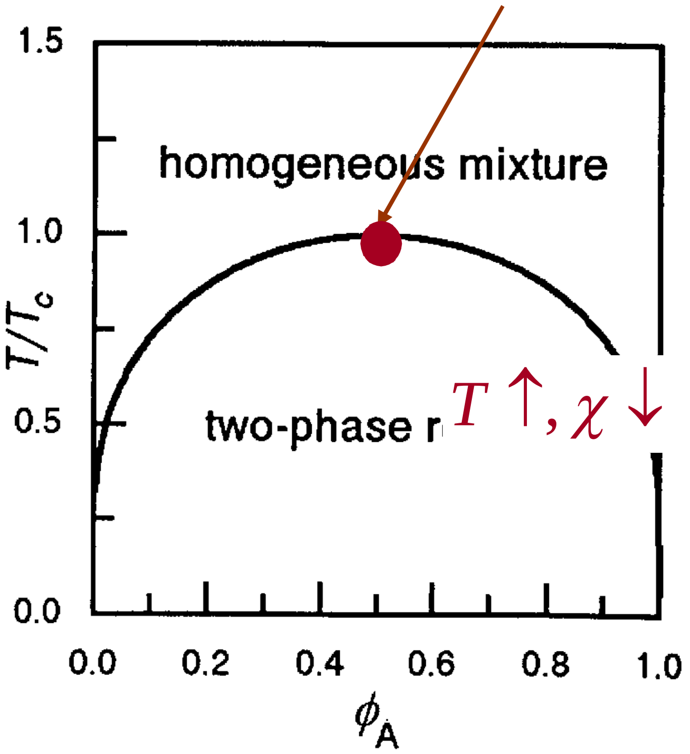


UCST / LCST

$$\Delta G = \chi \phi_1 \phi_2 - T \Delta S \qquad \chi = \frac{A}{T}$$

Upper critical solution temperature (UCST)

$A > 0$



$T \uparrow, \chi \downarrow$

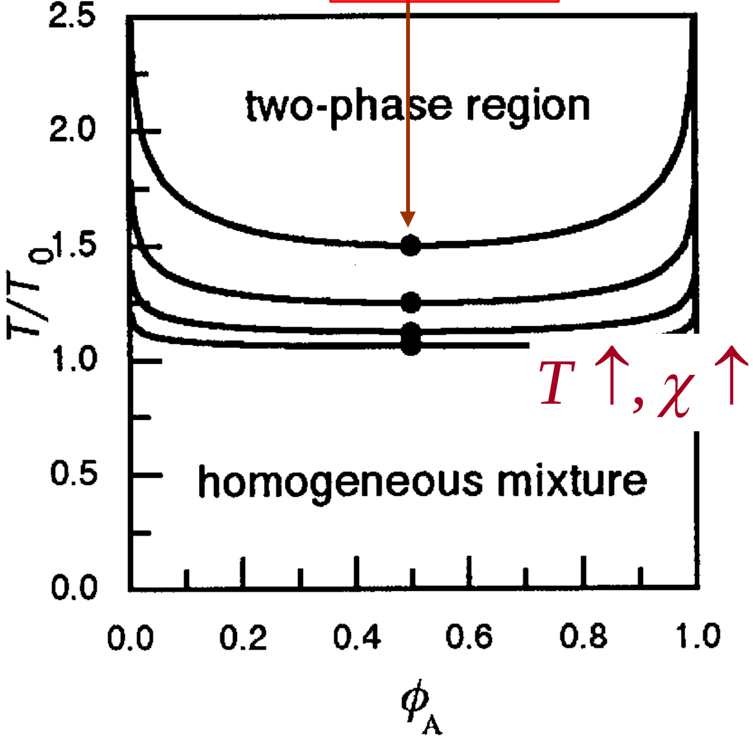
Endothermic symmetrical polymer mixture

Lower critical solution temperature (LCST)

$A < 0$

$$\boxed{\chi = \frac{A}{T} + B}$$

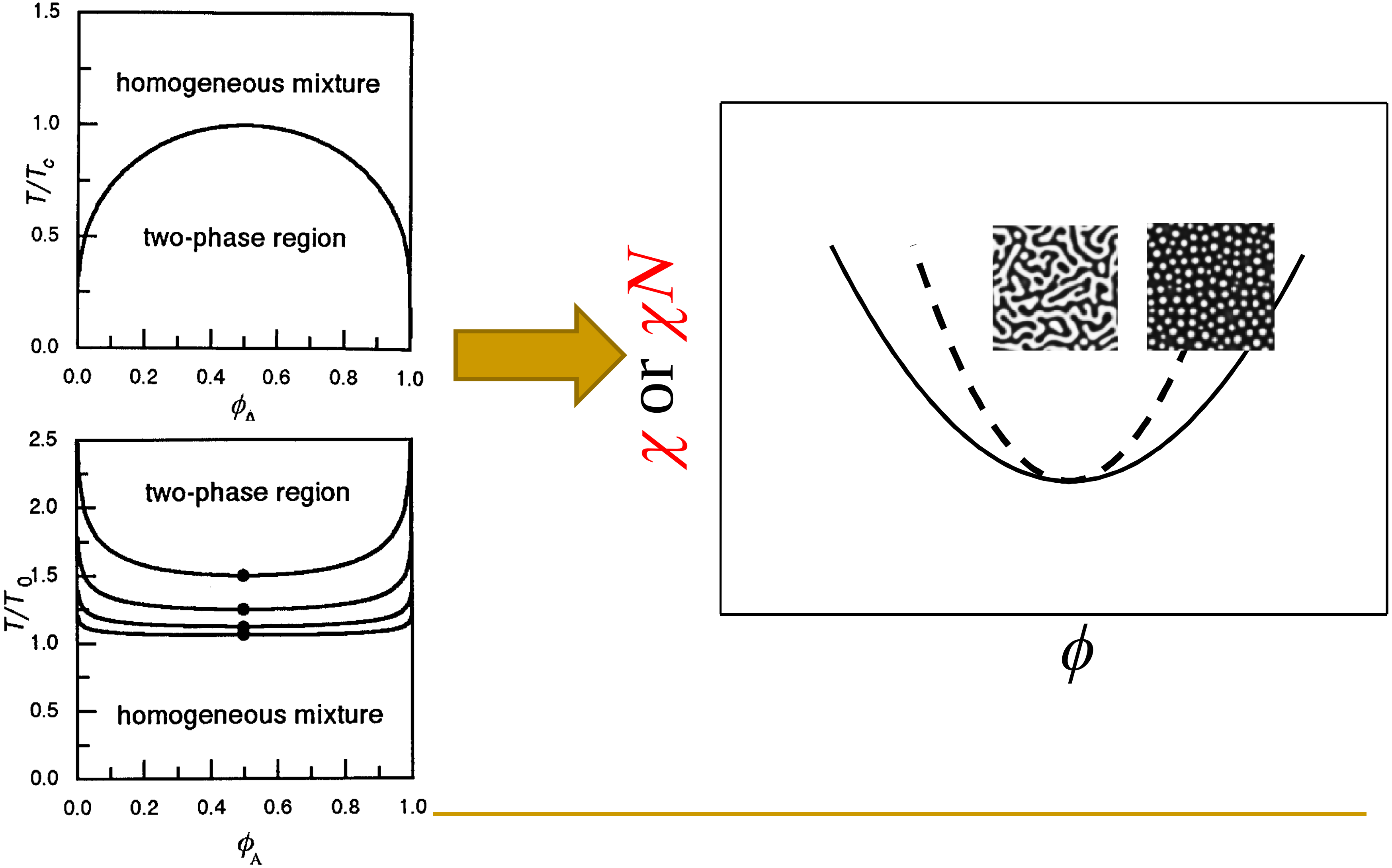
$B > 0$



$T \uparrow, \chi \uparrow$

Exothermal symmetrical polymer mixture

Universal Phase Diagram



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}:**

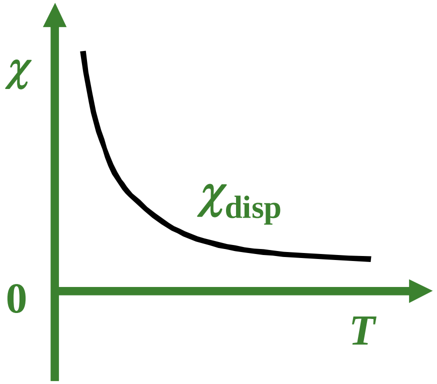
Dispersion forces

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

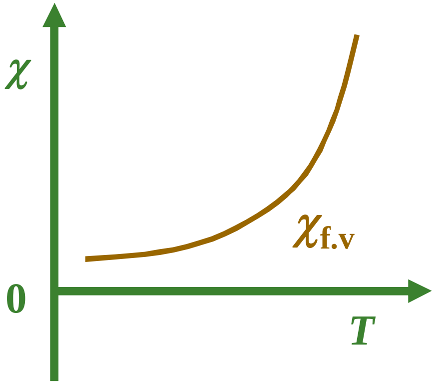
Specific interactions

$A>0$ UCST

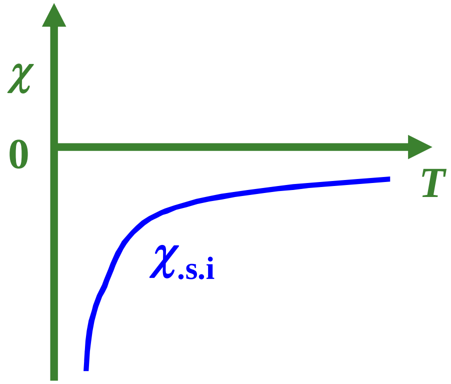
$A<0$ LCST



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



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

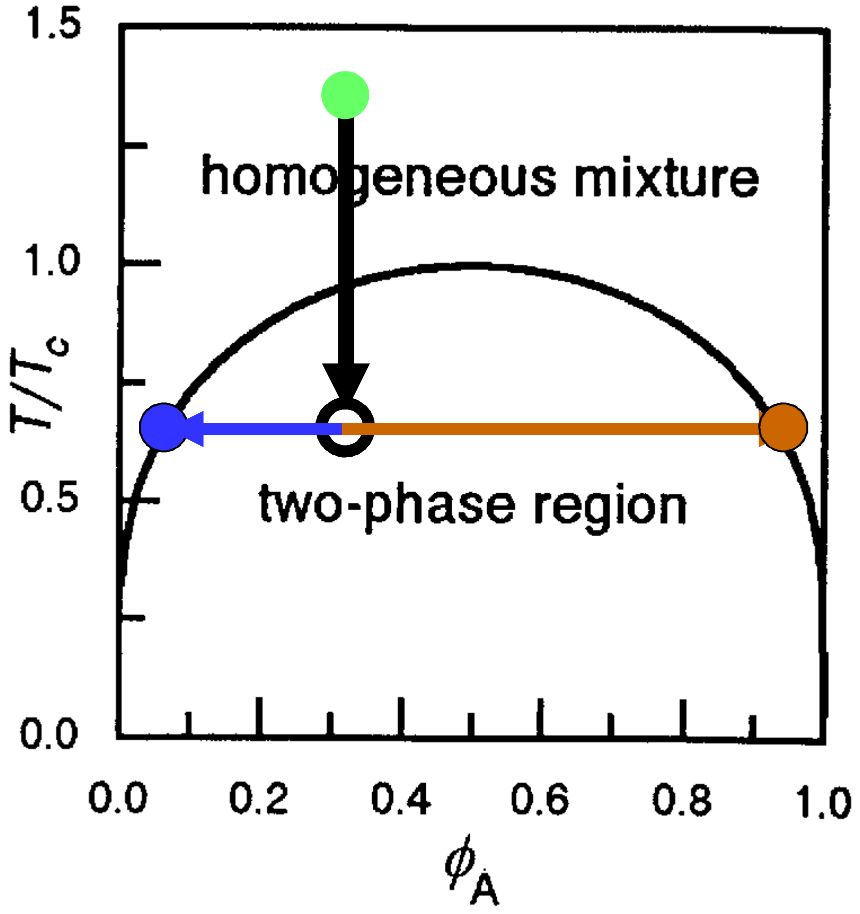


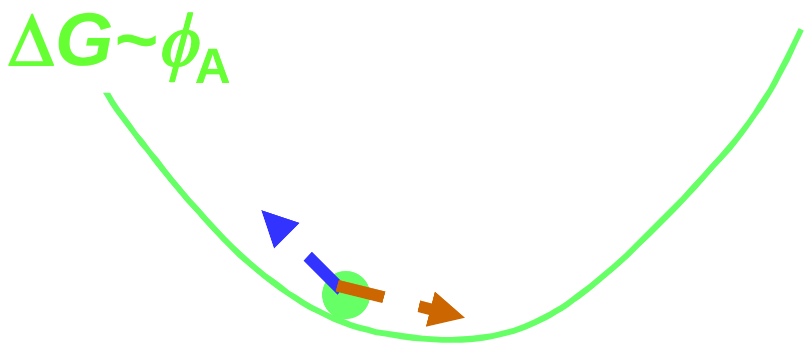
Specific interaction:
Always < 0, decreasing
magnitude with increasing T.

The Phase Behavior of Polymer Mixtures

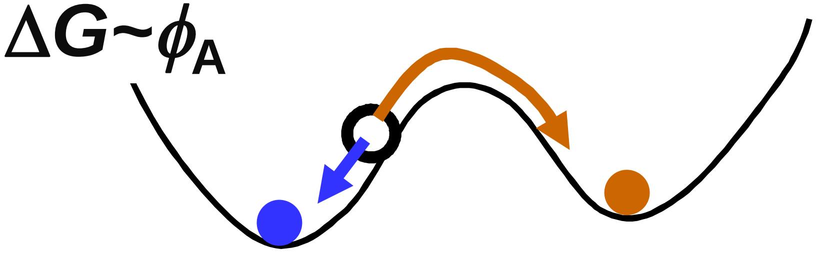
How to judge it‘s homogeneous state or inhomogeneous state ?

What is the mechanism of phase separation?



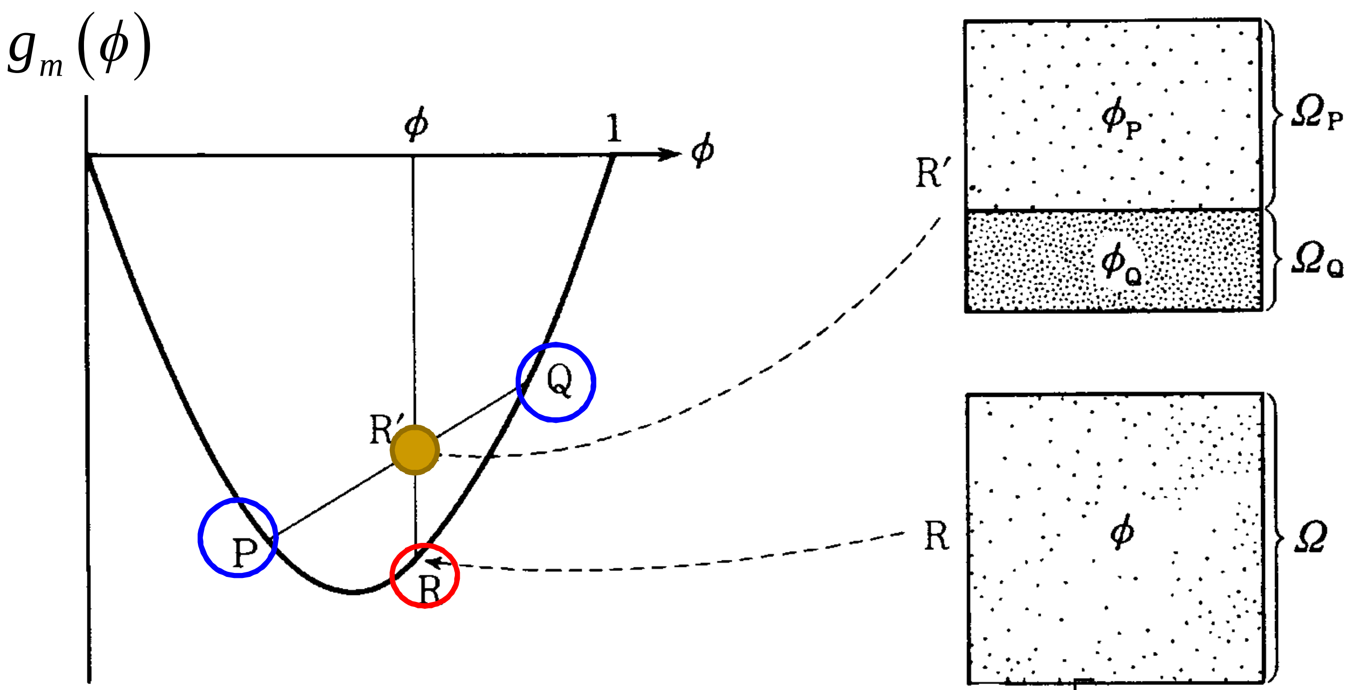


$$V_1 \Delta g_1 + (1-V_1)\Delta g_2 - \Delta G > 0$$



$$V_1 \Delta g_1 + (1-V_1)\Delta g_2 - \Delta G < 0$$

The shape of the mixing free energy curve with one local minimum



$$\Omega_P\phi_P + \Omega_Q\phi_Q = \Omega\phi$$

$$\Omega_P + \Omega_Q = \Omega$$

$$\Omega_P = \frac{\phi_Q - \phi}{\phi_Q - \phi_P}\Omega$$

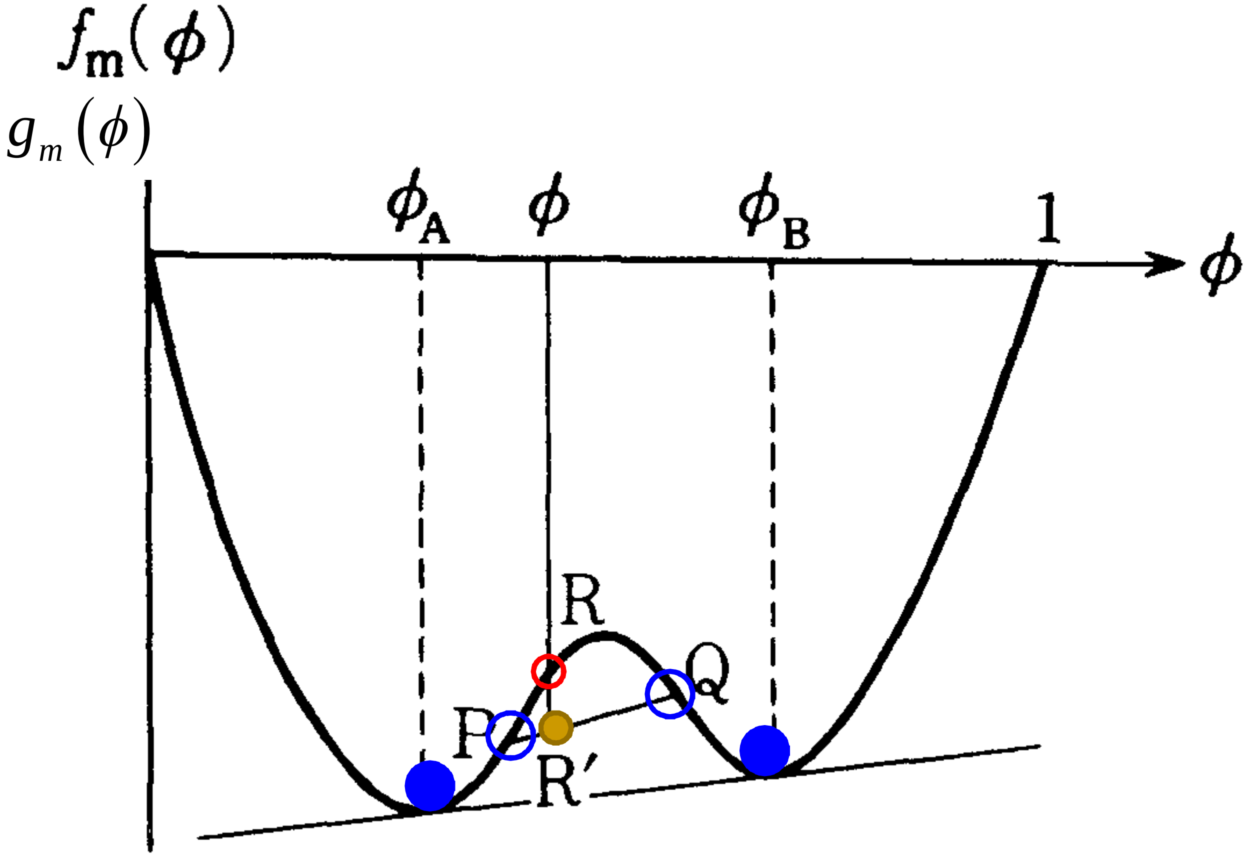
$$\Omega_Q = \frac{\phi - \phi_P}{\phi_Q - \phi_P}\Omega$$

$$\Delta G_{mix} = kT\left[\Omega_P g_m(\phi_P) + \Omega_Q g_m(\phi_Q)\right] = \Omega kT\left[\frac{\phi_Q - \phi}{\phi_Q - \phi_P} g_m(\phi_P) + \frac{\phi - \phi_P}{\phi_Q - \phi_P} g_m(\phi_Q)\right]$$

$$= \Delta G(R') > \Delta G(R)$$

Phase Separation will not occur if free energy curve has one local minimum

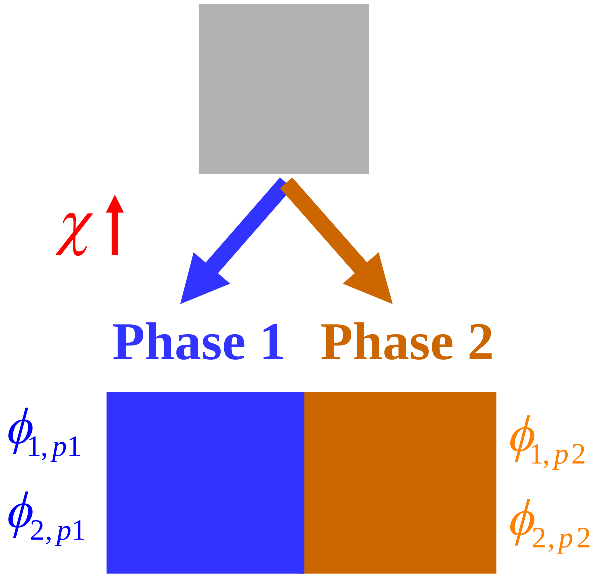
Free energy curve with two local minima



Phase Separation can take place if free energy curve has two local minima

$$\left[\frac{\partial g_m(\phi)}{\partial \phi}\right]_{\phi_A} = \left[\frac{\partial g_m(\phi)}{\partial \phi}\right]_{\phi_B} = \frac{g_m(\phi_B) - g_m(\phi_A)}{\phi_B - \phi_A}$$

Phase Diagram and Phase Equilibrium

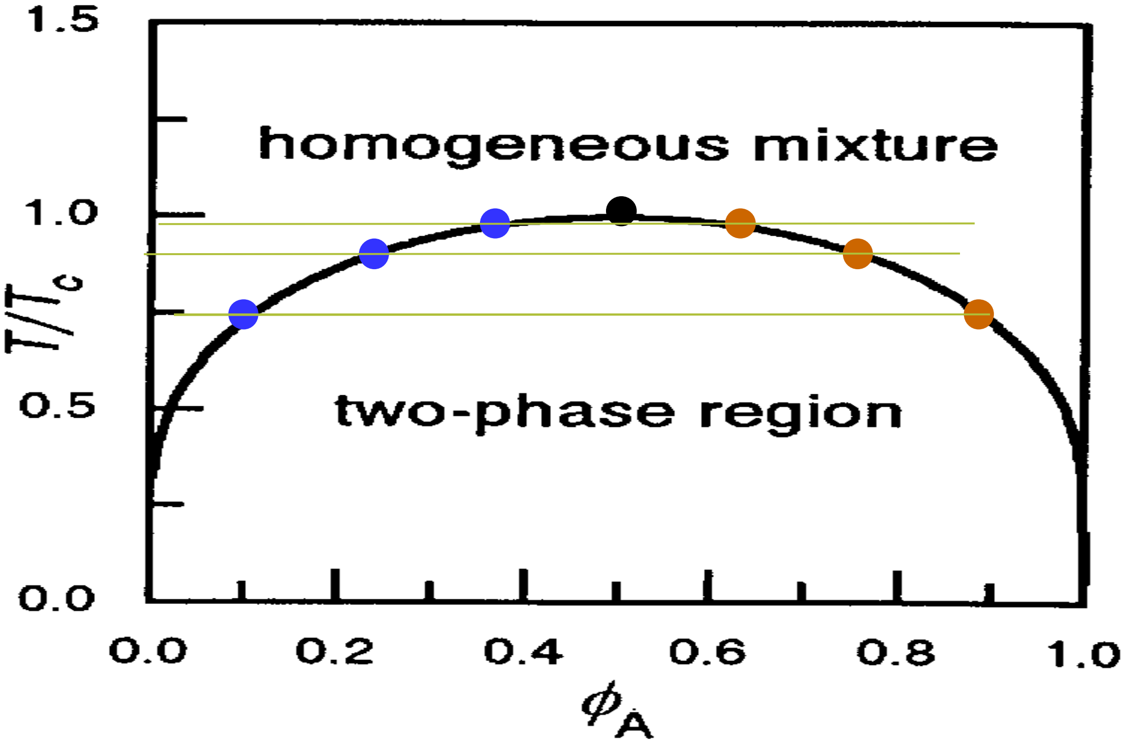


$\chi \uparrow$

Phase 1 **Phase 2**

$\phi_{1,p1}$ $\phi_{2,p1}$

$\phi_{1,p2}$ $\phi_{2,p2}$



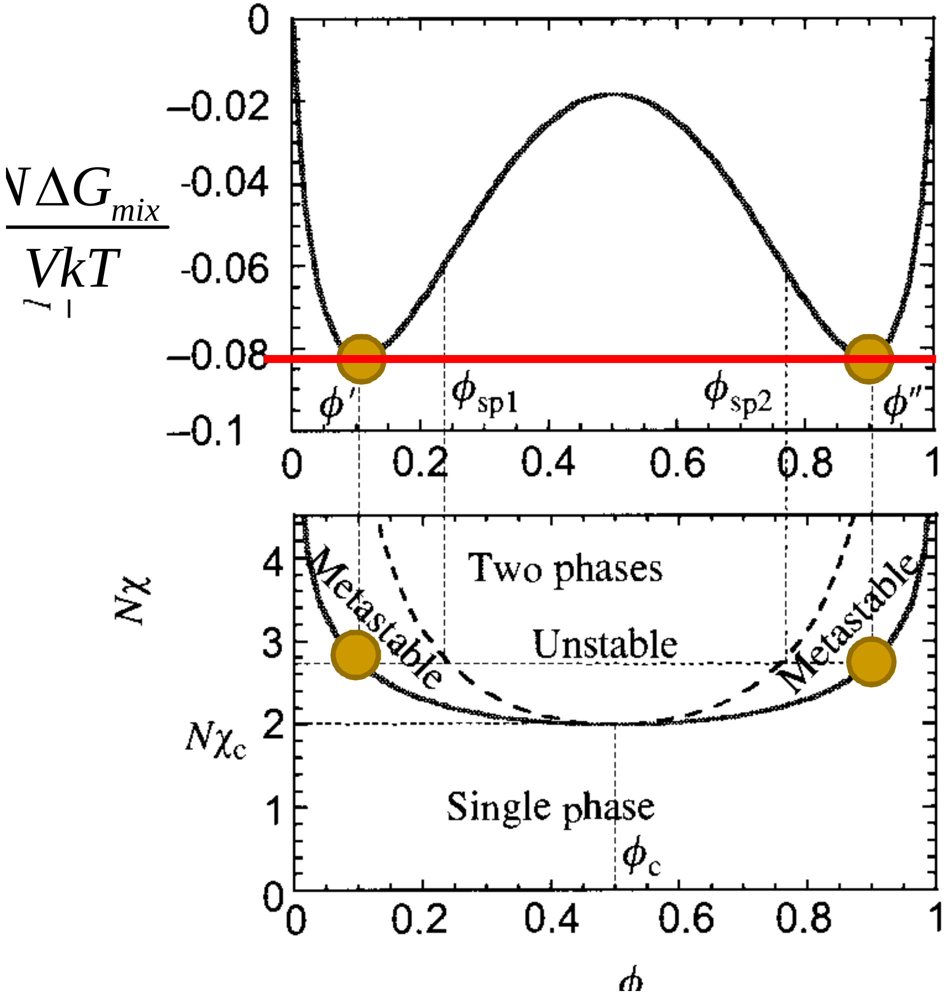
$$\left.\begin{array}{l}\Delta\mu_{1,p1} = \Delta\mu_{1,p2}\\ \Delta\mu_{2,p1} = \Delta\mu_{2,p2}\\ \phi_{1,p1}+\phi_{2,p1}=1\\ \phi_{1,p2}+\phi_{2,p2}=1\end{array}\right\} \rightarrow$$

$$\ln\left(1-\phi_{2,p1}\right)+\left(1-\frac{x_1}{x_2}\right)\phi_{2,p1}+x_1\chi\left(\phi_{2,p1}\right)^2=\ln\left(1-\phi_{2,p2}\right)+\left(1-\frac{x_1}{x_2}\right)\phi_{2,p2}+x_1\chi\left(\phi_{2,p2}\right)^2$$

$$\ln\phi_{2,p1}+\left(1-\frac{x_2}{x_1}\right)\left(1-\phi_{2,p1}\right)+x_2\chi\left(1-\phi_{2,p1}\right)^2=\ln\phi_{2,p2}+\left(1-\frac{x_2}{x_1}\right)\left(1-\phi_{2,p2}\right)+x_2\chi\left(1-\phi_{2,p2}\right)^2$$

I. Phase diagram of symmetric mixtures

$$\Delta G_{mix} = RTV\left(\frac{\phi}{N}\ln\phi + \frac{1-\phi}{N}\ln(1-\phi) + \chi\phi(1-\phi)\right) \qquad \frac{\partial \Delta G_{mix}}{\partial \phi} = 0$$



$$= RTV\left(\frac{\ln\phi}{N} + \frac{1}{N} - \frac{\ln(1-\phi)}{N} - \frac{1}{N} + \chi_b(1-2\phi)\right)$$

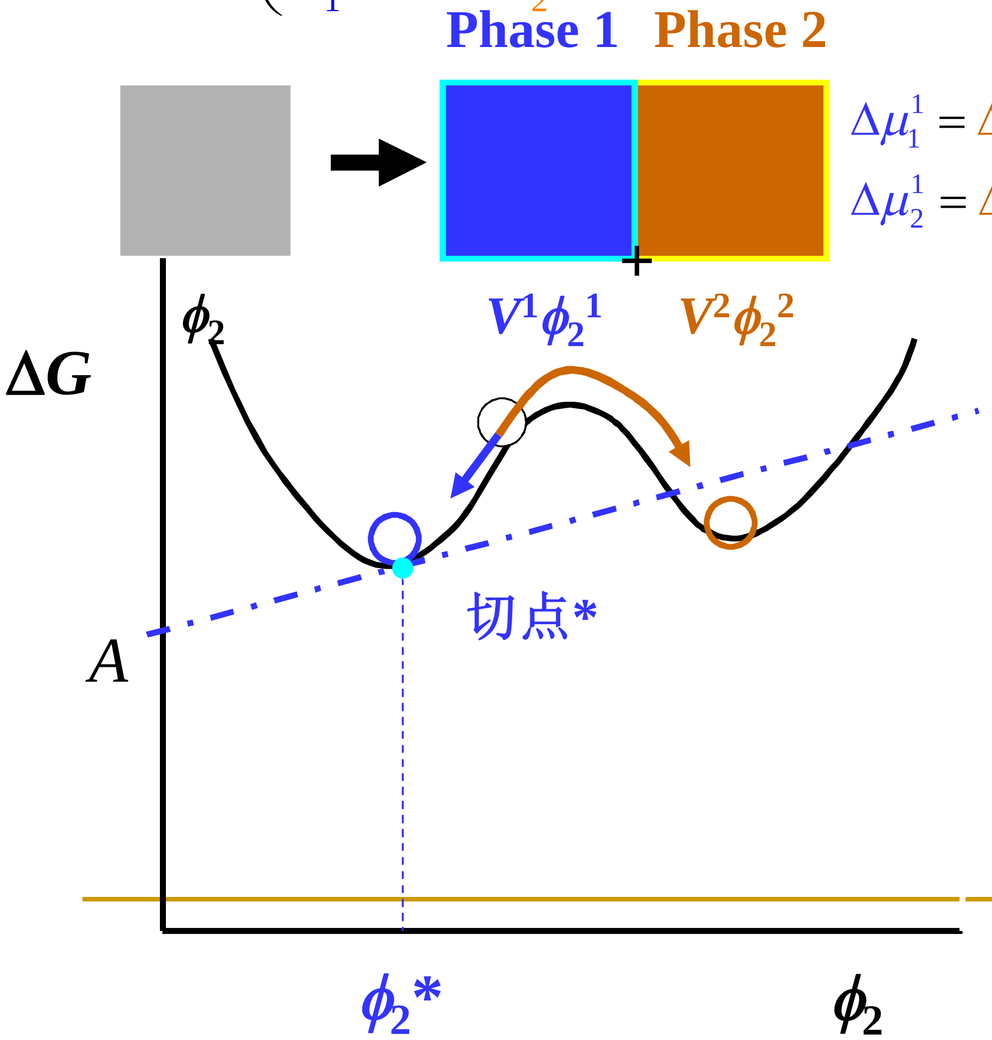
$$= RTV\left(\frac{1}{N}\ln\frac{\phi}{(1-\phi)} + \chi_b(1-2\phi)\right) = 0$$

$$\boxed{\chi_b N = \frac{1}{(2\phi-1)}\frac{\ln\phi}{\ln(1-\phi)}} \qquad \chi_b = \frac{A}{T_b} + B$$

$$\boxed{T_b = \frac{A}{\frac{1}{N(2\phi-1)}\ln\frac{\phi}{(1-\phi)} - B}}$$

II. Phase diagram of asymmetric mixtures

$$\Delta G_{mix} = RTV\left(\frac{\phi}{N_1}\ln\phi + \frac{1-\phi}{N_2}\ln(1-\phi) + \chi\phi(1-\phi)\right)$$



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

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

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

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

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

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

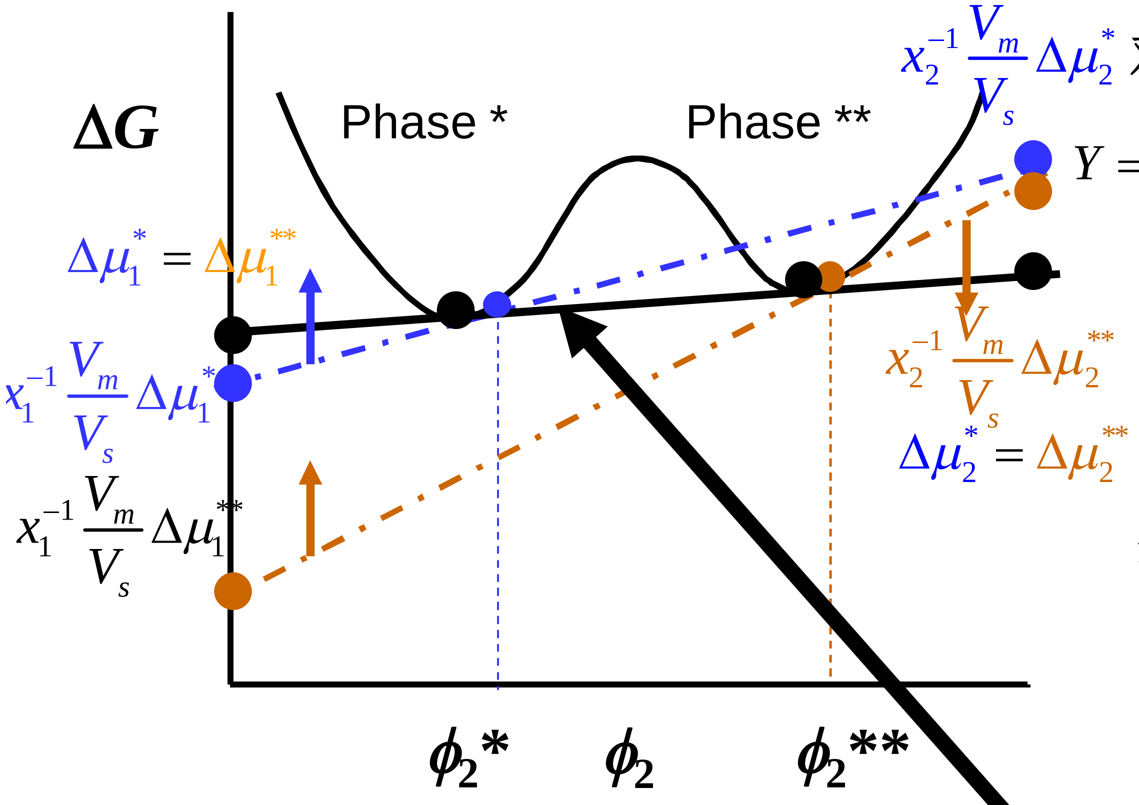
$$= \frac{V_m}{V_s}\left[x_1^{-1}\Delta\mu_1 + \phi_2\left(x_2^{-1}\Delta\mu_2 - x_1^{-1}\Delta\mu_1\right)\right]$$

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



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 $\Delta\mu_1^1 = \Delta\mu_1^2$, $\Delta\mu_2^1 = \Delta\mu_2^2$ 相平衡条件满足

必须作一根这样的切线满足

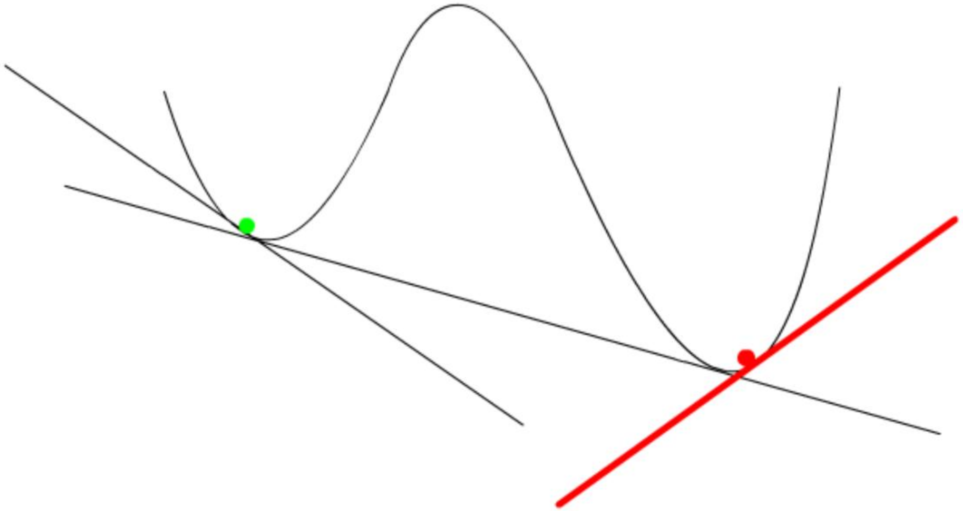
$$\Delta\mu_1^* = \Delta\mu_1^{**}$$

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

唯有同时通过两个切点的共切线才能满足相平衡条件

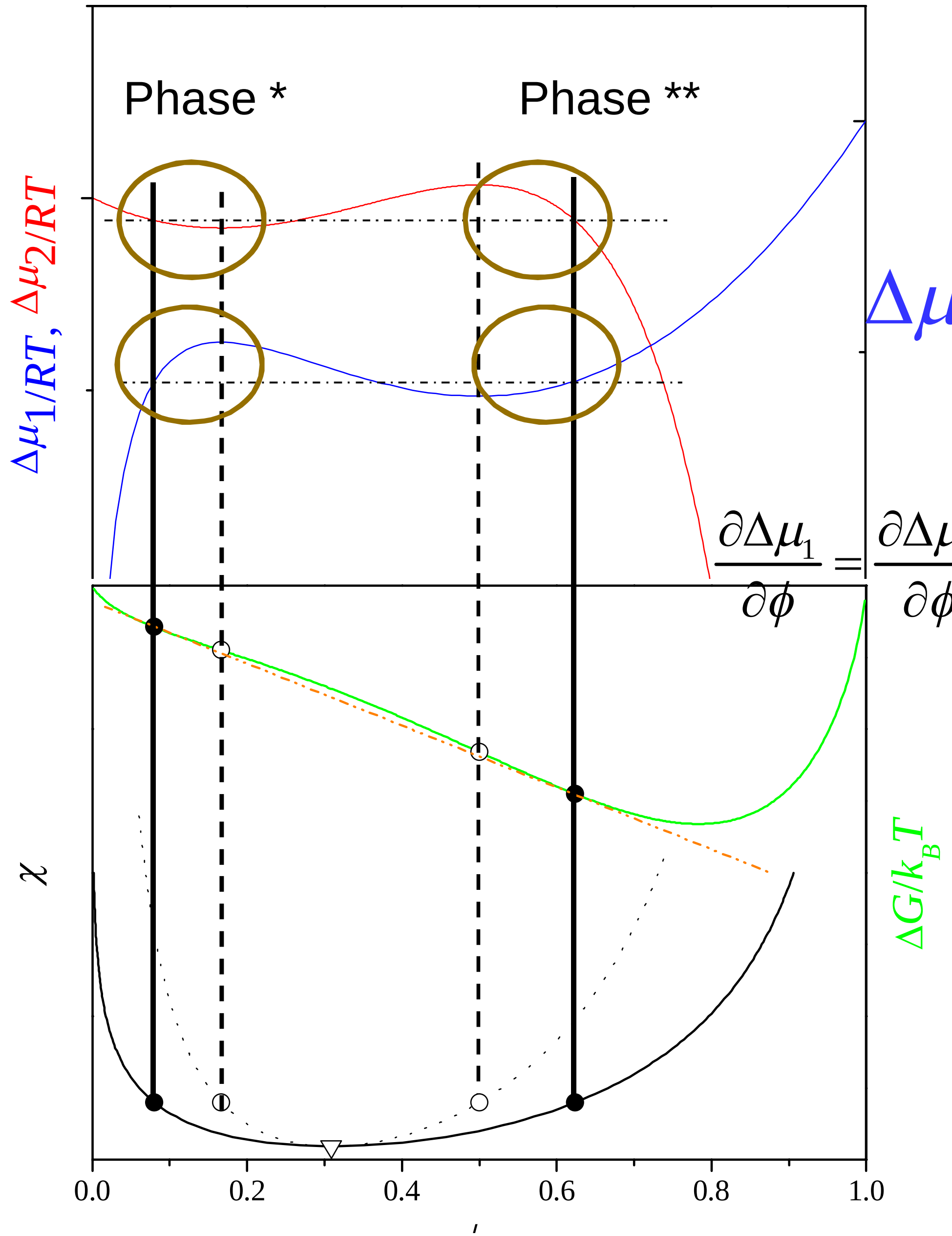
Search the phase equilibrium point

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



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

Relations between Free Energy， Chemical Potentials and Phase Diagram



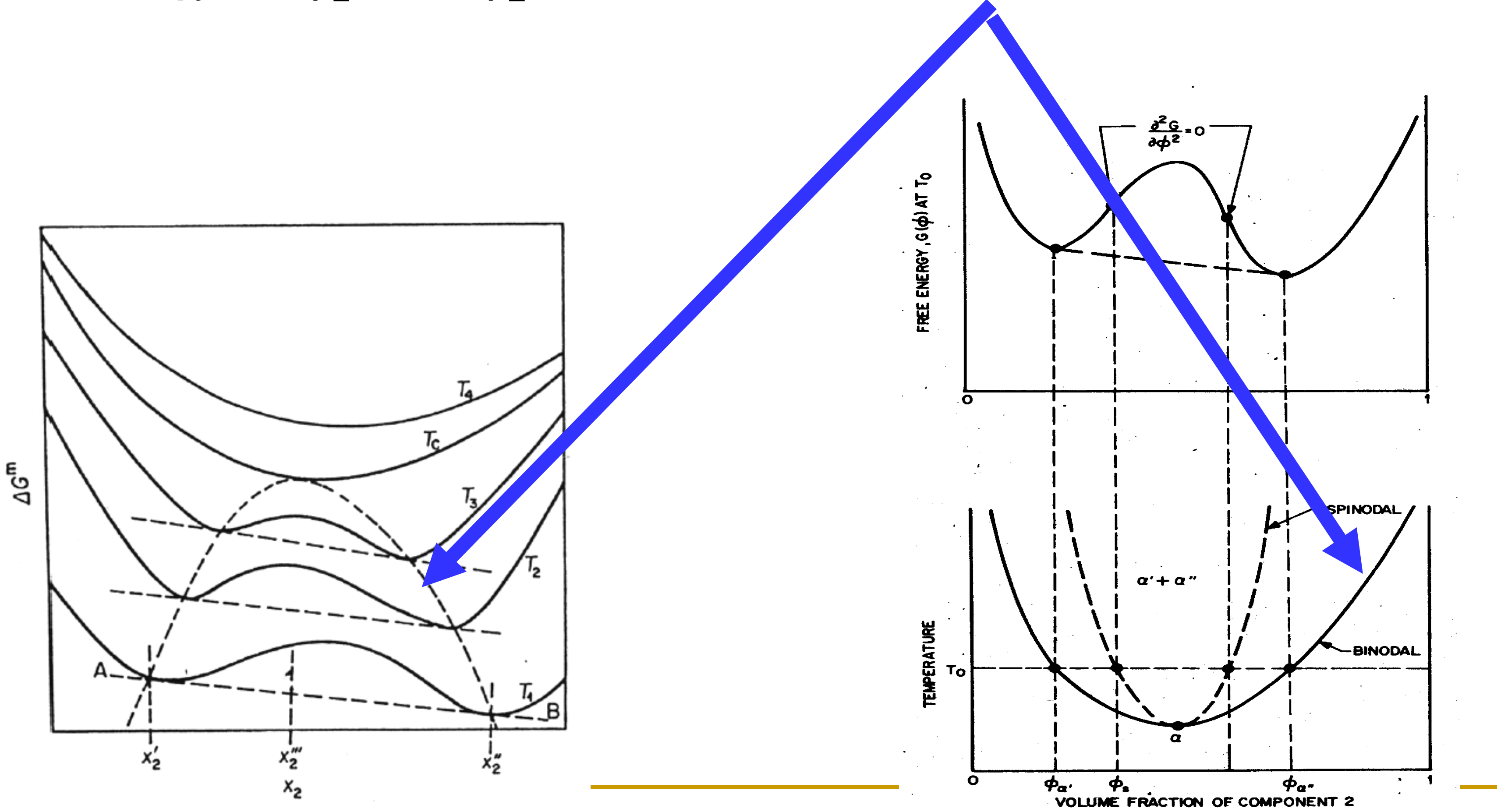
$$\Delta\mu_1^{*} = \Delta\mu_1^{**}$$

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

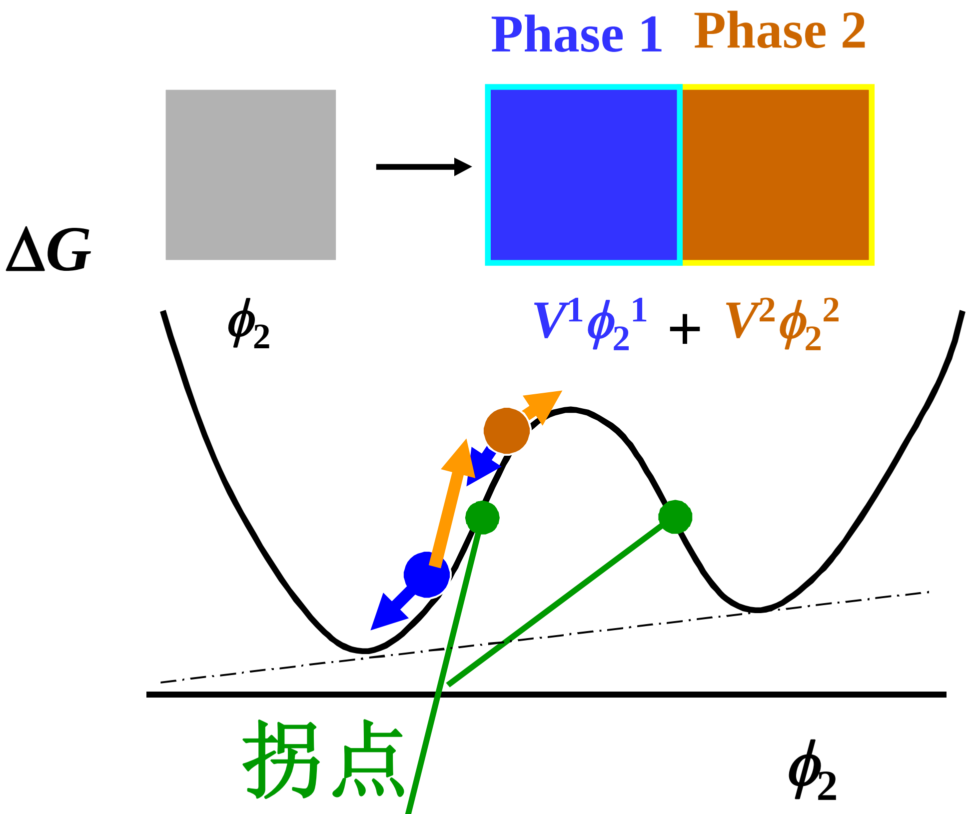
$$\frac{\partial \Delta\mu_1}{\partial\phi} = \frac{\partial \Delta\mu_2}{\partial\phi} = \frac{\partial^2 \Delta G}{\partial\phi^2} = 0$$

(1) Phase equilibrium curve – binodal

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



(2) Metastable/unstable limits - spinodal



Phase 1 **Phase 2**

ΔG

ϕ_2

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

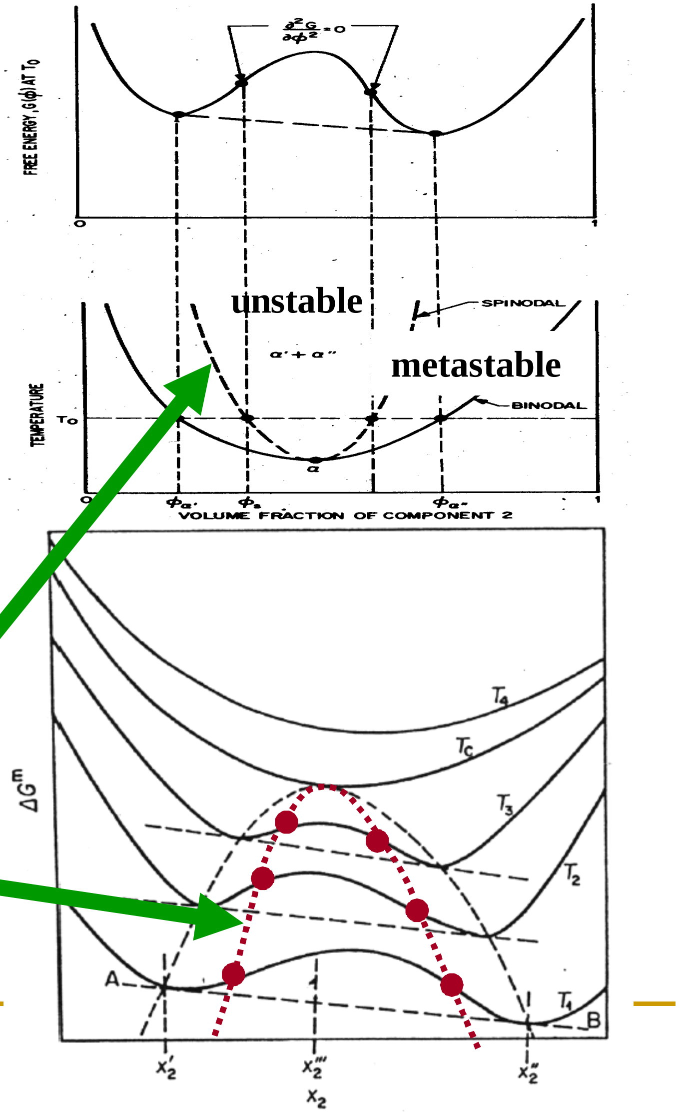
拐点

ϕ_2

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

Spinodal curve

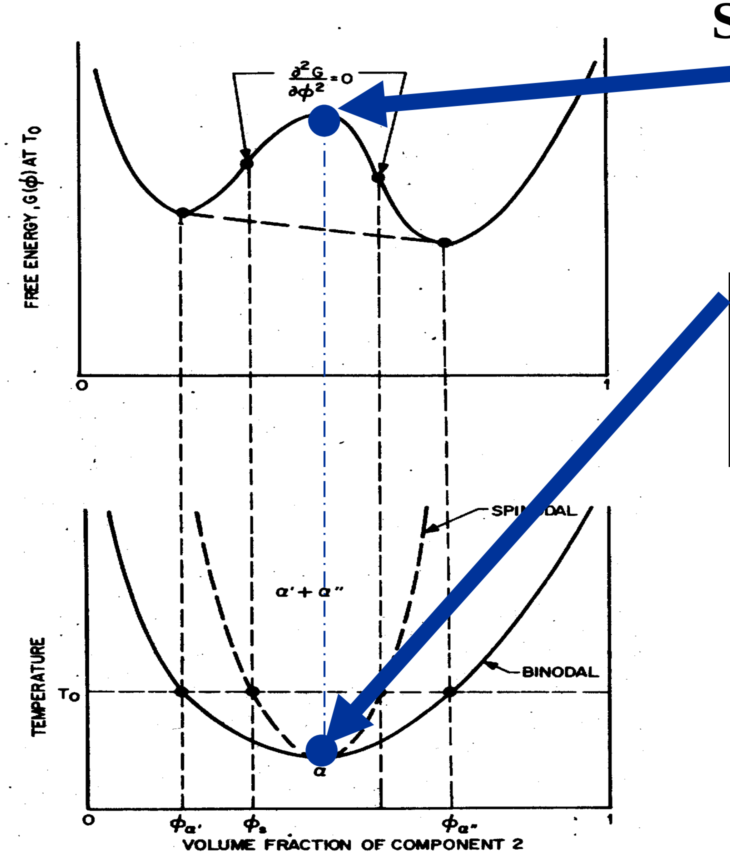
$$\boxed{\frac{\partial^2 \Delta G}{\partial \phi_2^2} = \frac{1}{x_1\left(1-\phi_2\right)} + \frac{1}{x_2\phi_2} - 2\chi = 0}$$



unstable

metastable

(3) Critical point



Spinodal 和 binodal的交点: Critical point

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

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

For symmetric blends x_1=x_2

$$\chi_c N = 2$$

For polymer solutions

$$\chi_c \to \frac{1}{2}$$

For symmetric di-blocks f=0.5

$$\chi_c N = 10.5$$

Critical points dependence of *N*

For blends

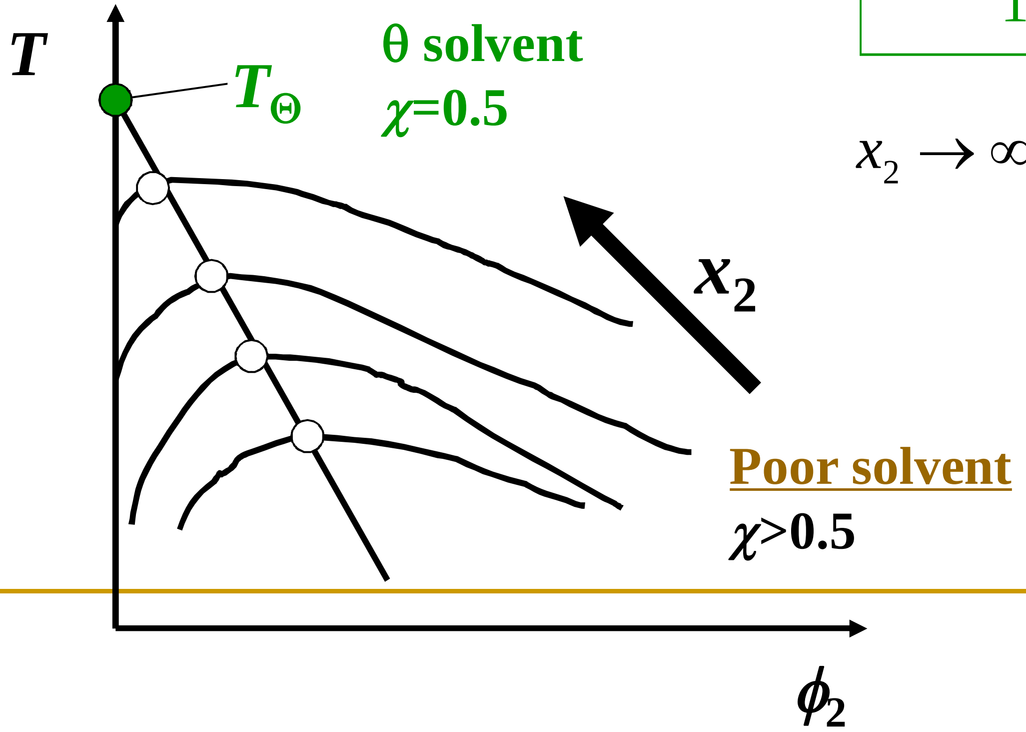
$$\phi_{2,c} = \frac{x_1^{1/2}}{x_1^{1/2}+x_2^{1/2}}, \quad \chi_c = \frac{1}{2}\left(\frac{1}{x_1^{1/2}}+\frac{1}{x_2^{1/2}}\right)^2$$

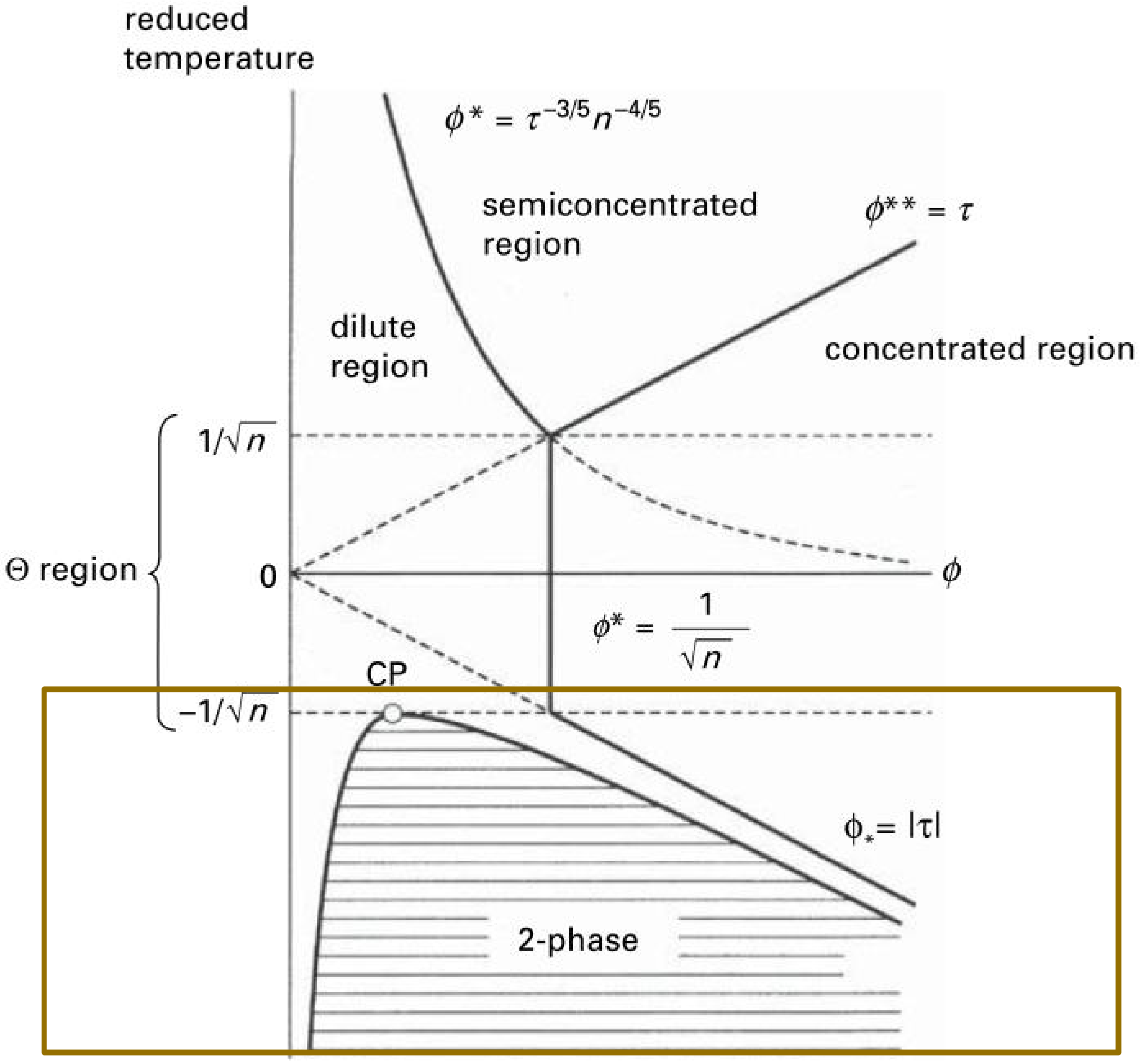
$$x\uparrow \to \chi_c\downarrow, \quad T_c\uparrow$$

For solutions

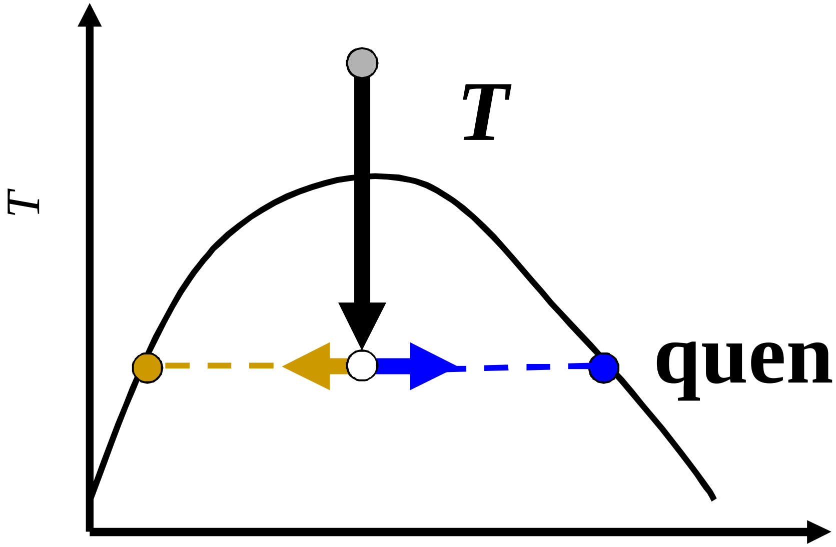
$$\phi_{2,c} = \frac{1}{1+x_2^{1/2}}, \quad \chi_c = \frac{1}{2}\left(1+\frac{1}{x_2^{1/2}}\right)^2$$

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




reduced temperature
$\phi^* = \tau^{-3/5} n^{-4/5}$
semiconcentrated region
$\phi^{**} = \tau$
dilute region
concentrated region
$1/\sqrt{n}$
Θ region
0
ϕ
$\phi^* = \frac{1}{\sqrt{n}}$
CP
$-1/\sqrt{n}$
$\phi_* = |\tau|$
2-phase

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

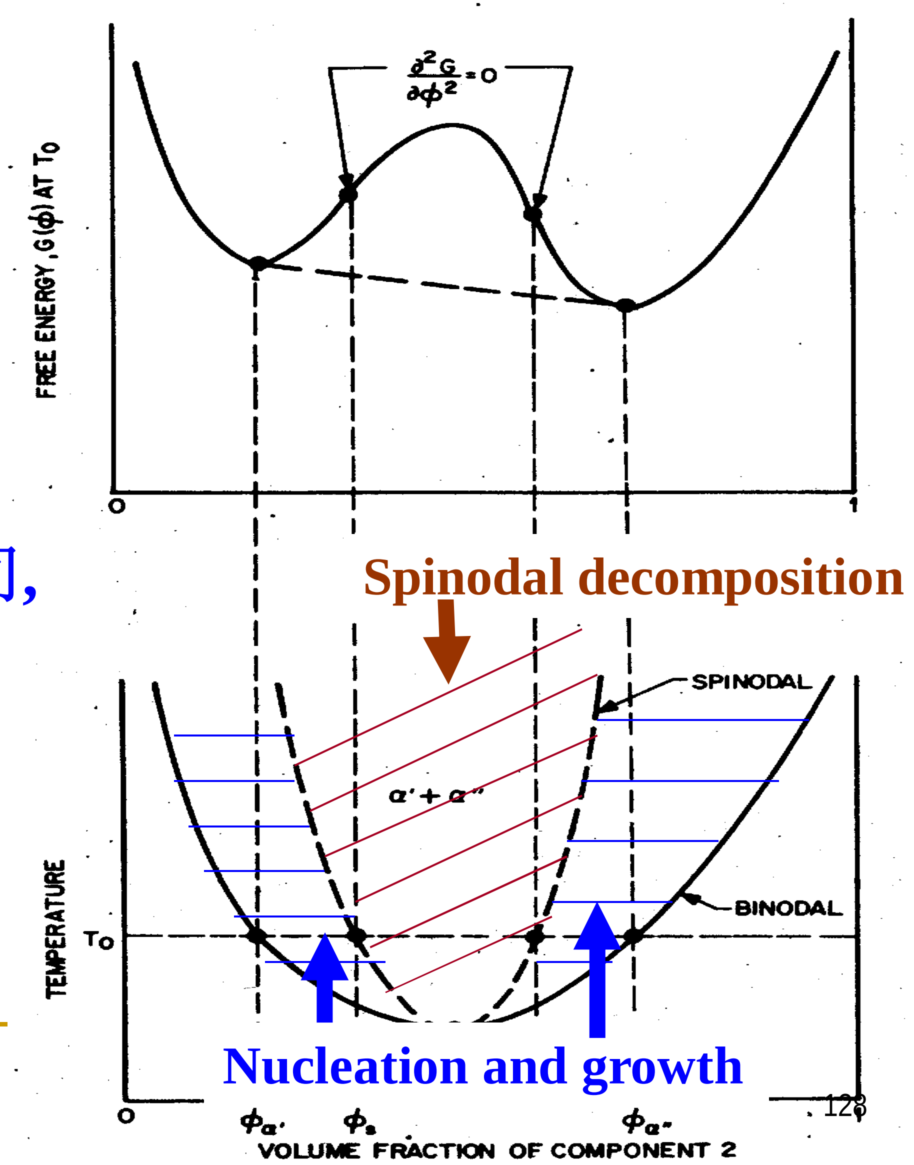
- **(1) 在临界组成附近, 不稳区, spinodal decomposition**
- **(2) 在相平衡线和spinodal线之间, 亚稳区, nucleation and growth**

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

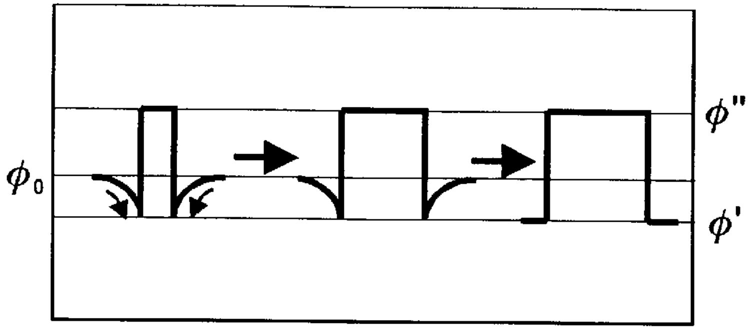


Spinodal decomposition

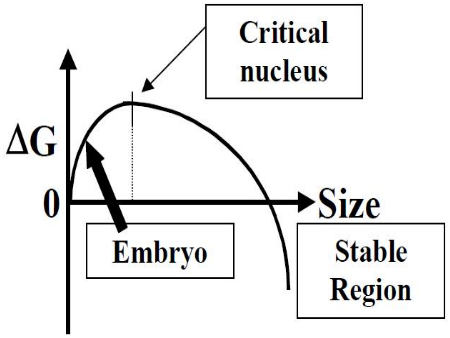
Nucleation and growth

Phase Separation Mechanisms

1. Nucleation and growth (成核生长) mechanism

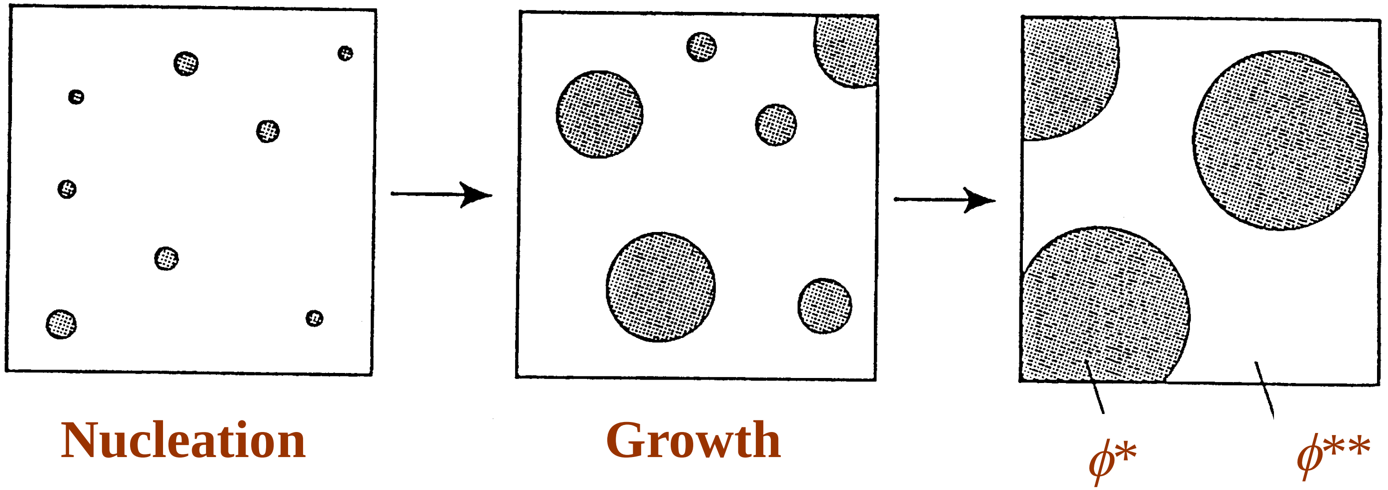


In metastable region, separation can proceed only by overcoming the barrier with a large fluctuation in composition.



Nucleation barrier: $\Delta G(r) = -\frac{4\pi}{3} r^3 \Delta g + 4\pi r^2 \gamma$ with $\Delta g = \Delta g(\varphi_0) - \Delta g(\varphi'')$

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

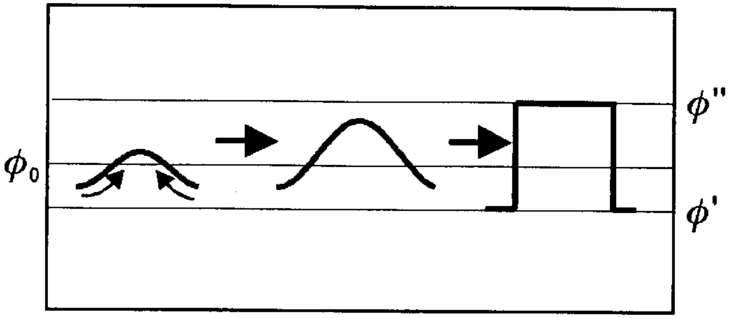


Nucleation **Growth**

droplet-dispersed phase

Phase Separation Mechanisms

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

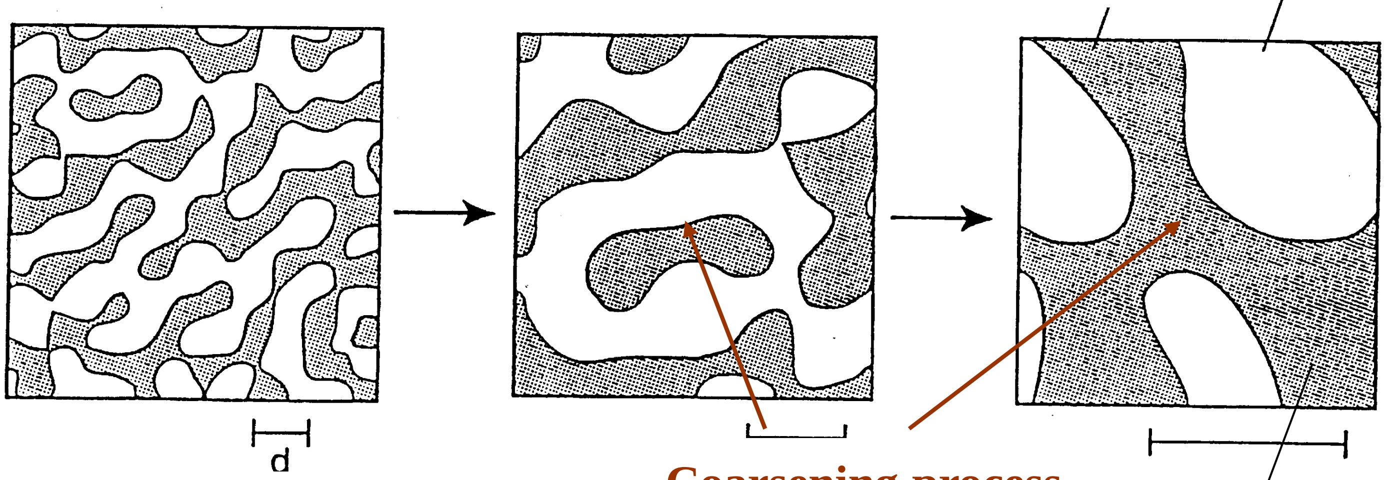


In unstable region, separation can occur spontaneously and continuously without any thermodynamic barrier.

Early stage
No sharp interface

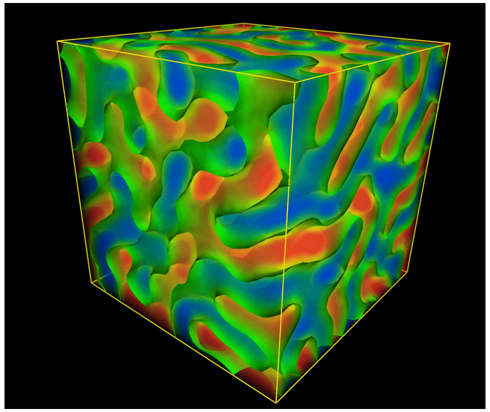
Late stage
Well-established interfaces

ϕ^{**}



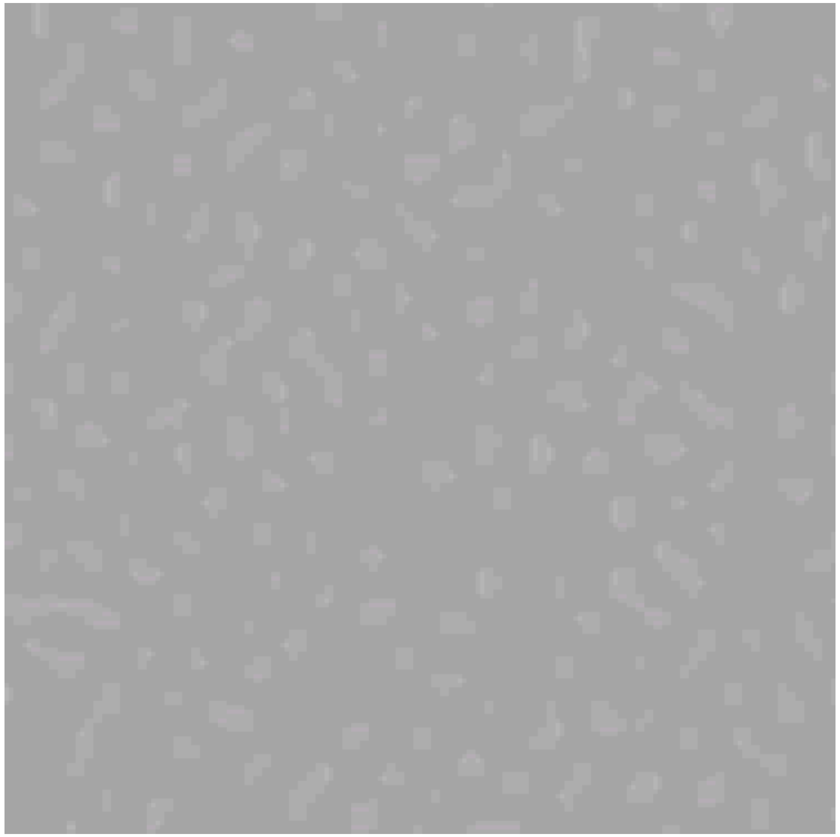
Coarsening process

ϕ^{*}

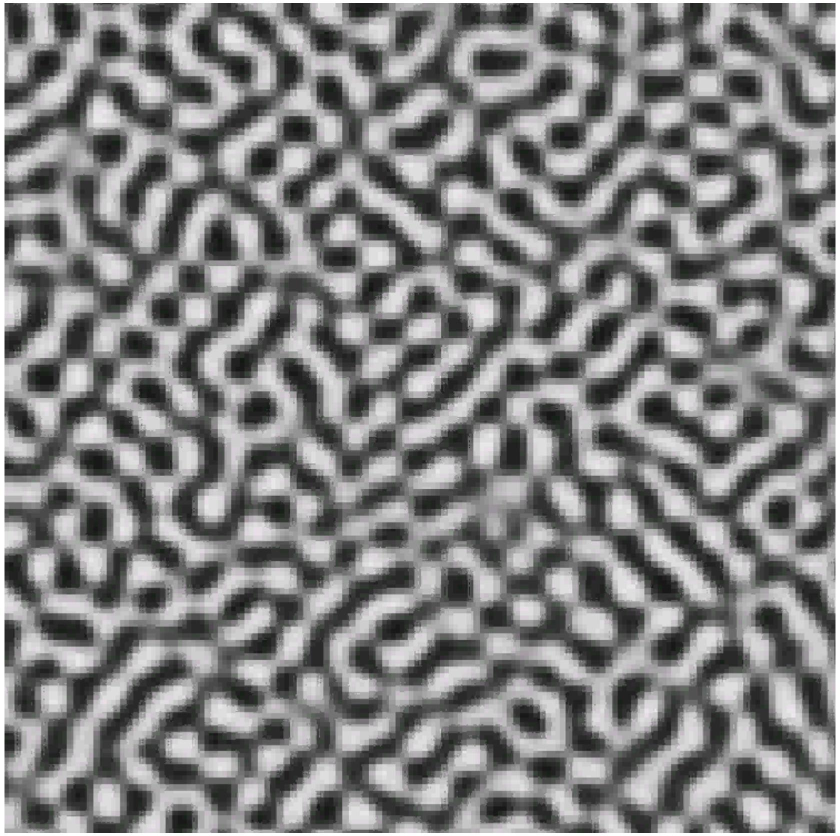


Co/bi-continuous phase

Examples of Phase Separation Dynamics

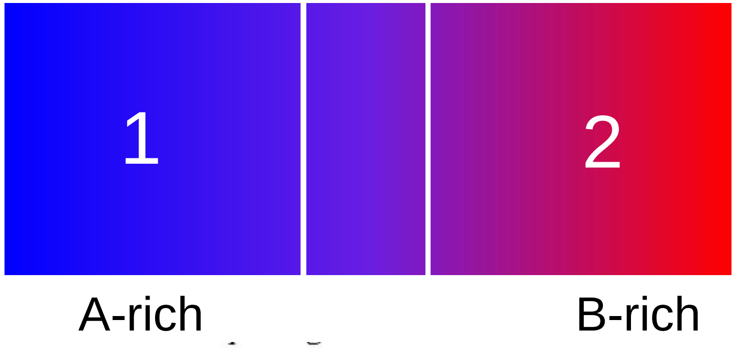


Nucleation & Growth



Spinodal Decomposition

Interfaces between weakly immiscible polymers

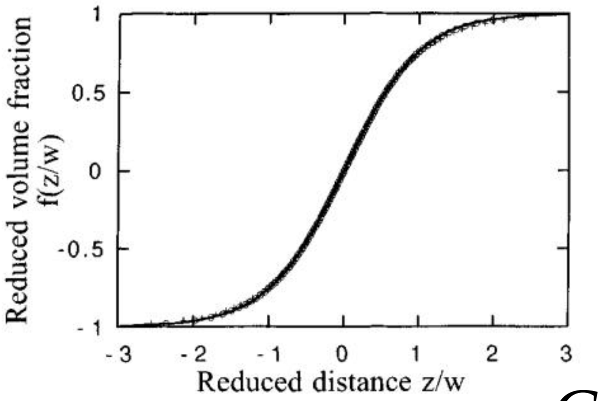


interfacial tension is defined as the increase in Gibbs free energy of the whole system per unit increase in interfacial area

$$\gamma = \left(\frac{\partial G}{\partial A} \right)_{T,p,n}$$

for each *i* phase

$$dG^i = -S^i dT + V^i dp + \mu_A dn_A^i + \mu_B dn_B^i$$



$$G^i = \mu_A n_A^i + \mu_B n_B^i$$

$$\mu_A^1 = \mu_A^2 = \mu_A^{\text{int}}$$

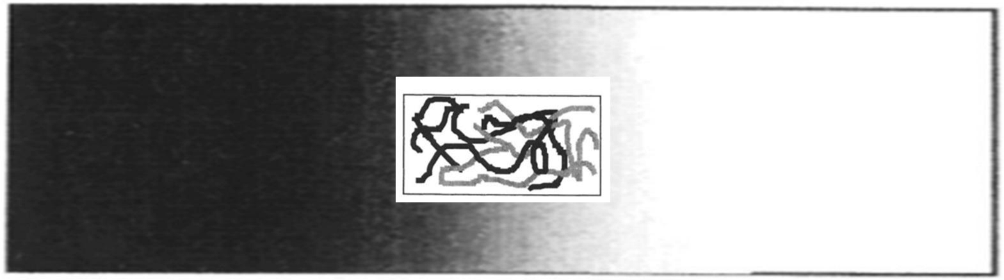
$$\mu_B^1 = \mu_B^2 = \mu_B^{\text{int}}$$

for interfacial region

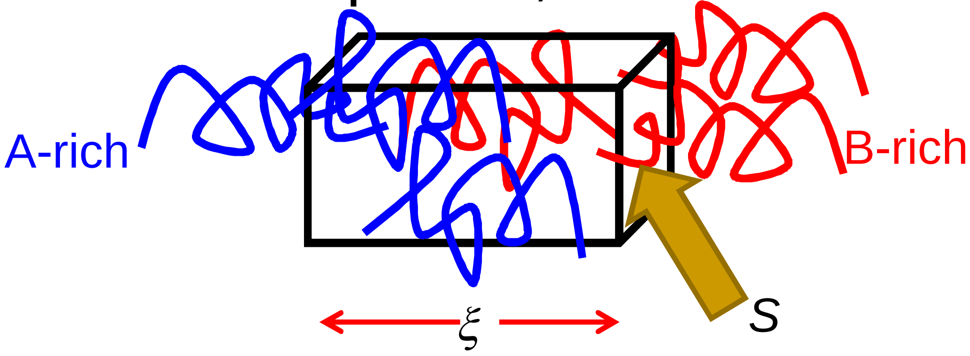
$$G^{\text{int}} = \gamma A + n_A^{\text{int}} \mu_A + n_B^{\text{int}} \mu_B$$

$$\gamma = \frac{G^{\text{int}}}{A} - \left(\Gamma_A \mu_A + \Gamma_B \mu_B \right)$$

$$\Gamma_A = \frac{n_A^{\text{int}}}{A} \qquad \Gamma_B = \frac{n_B^{\text{int}}}{A}$$



The width of the interface is determined by a balance of chain entropy, favoring a wider interface,
and the unfavorable energy of interaction between the two different species, which favors a narrow interface.



Suppose a loop of the A polymer with N_{loop} units protrudes into the B side of the interface

$$G_{loop} \approx N_{loop}\chi_{AB}k_BT \approx k_BT \qquad N_{loop}\chi_{AB} \approx 1$$

Interfacial width: $\xi \approx 2R_{g,loop} = \dfrac{2bN_{loop}^{1/2}}{\sqrt{6}}$ b: Kuhn segment $\qquad \xi \approx \dfrac{2b}{\sqrt{6\chi_{AB}}}$

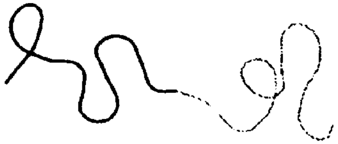
$$\gamma_{AB} = \rho_A V\chi_{AB}k_BT / S \qquad V = S\xi / 2$$

Segment density: $\rho_A = \dfrac{N}{Nb^3}$

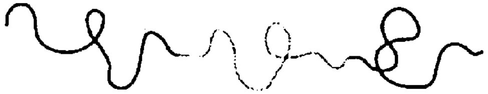
$$\boxed{\gamma_{AB} \approx \frac{k_BT}{b^2}\sqrt{\frac{\chi_{AB}}{6}}}$$

(Helfand, E.; Tagami, Y. ***JPS, PL***, **1971**, *9*, 741)

4.3 Theromodynamics of Block Copolymers

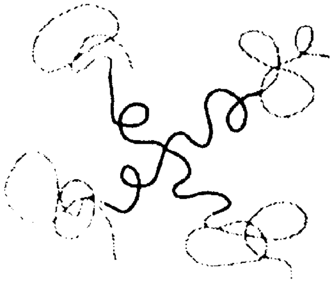


diblock

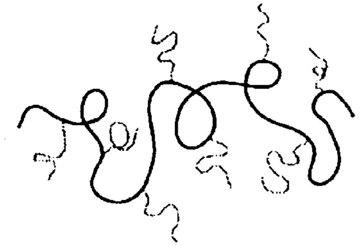


triblock

random multiblock



four arm starblock



graft copolymer

Applications:

Thermoplastics (热塑性弹性体)：PU, SBS

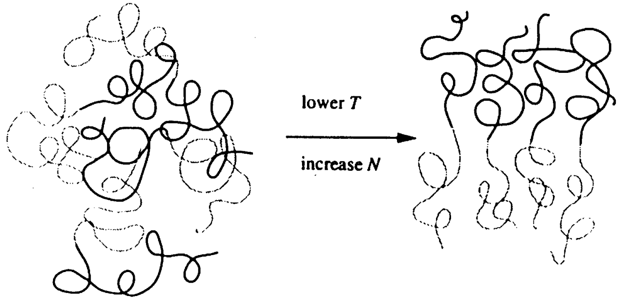
Compabilitzier (相容剂) of Polymer Blends

Nanotechnology, Biomaterials…

Self-assembly of Diblock Copolymers

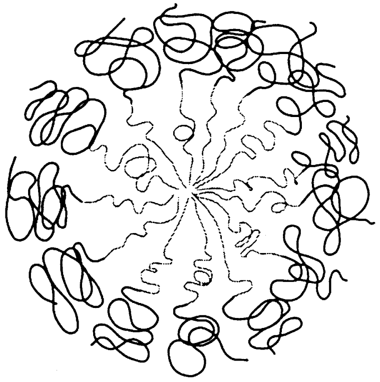
➢ Melts

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



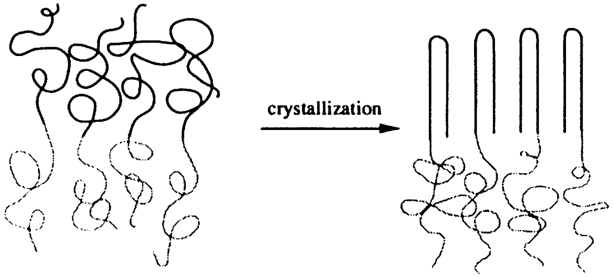
➢ Solutions

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 .



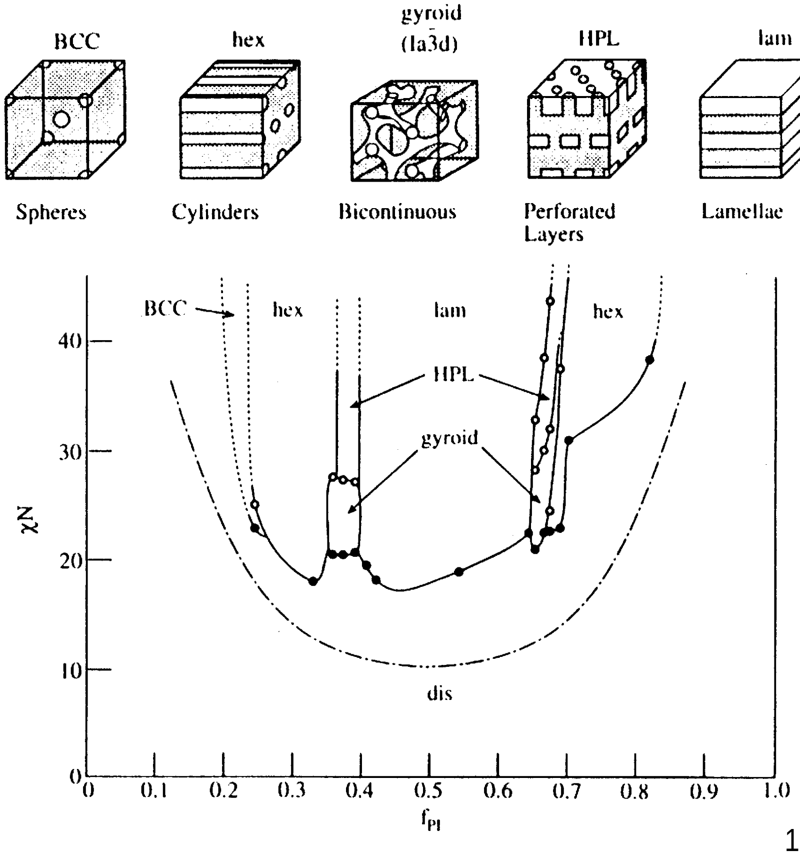
Microphase Separation of Diblock Copolymers (BCPs)

- **Phase diagram**

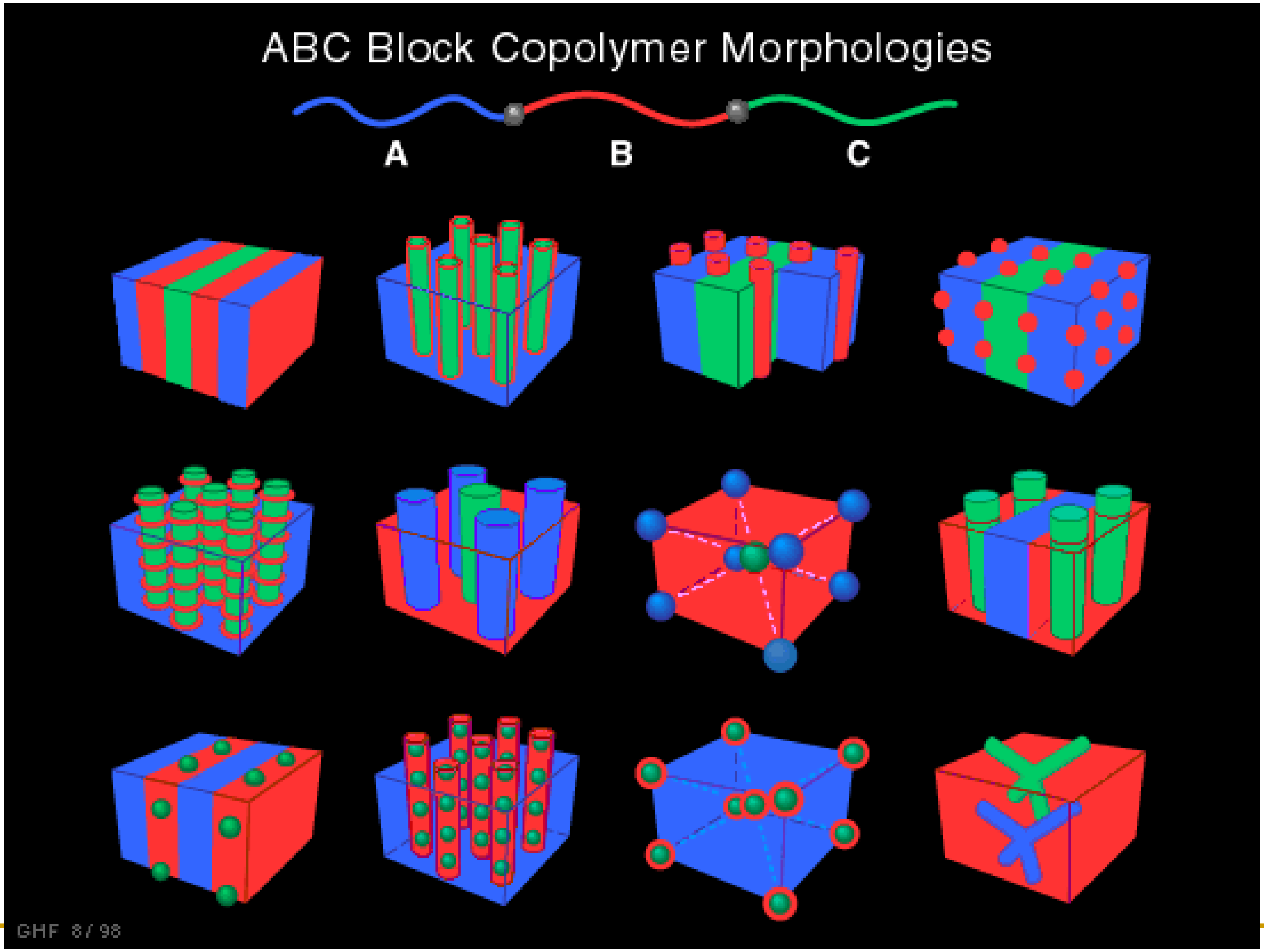
Homogeneous State → (order / disorder) → **Structurally Order State** → (order / order) → **Structurally Order State**

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

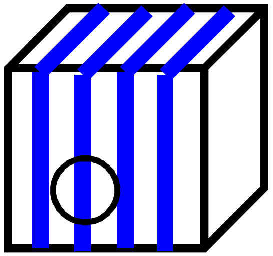
- **χN expresses the enthalpic-entropic balance. It is used to parameterize block copolymer phase behavior, along with the composition of the copolymer.**



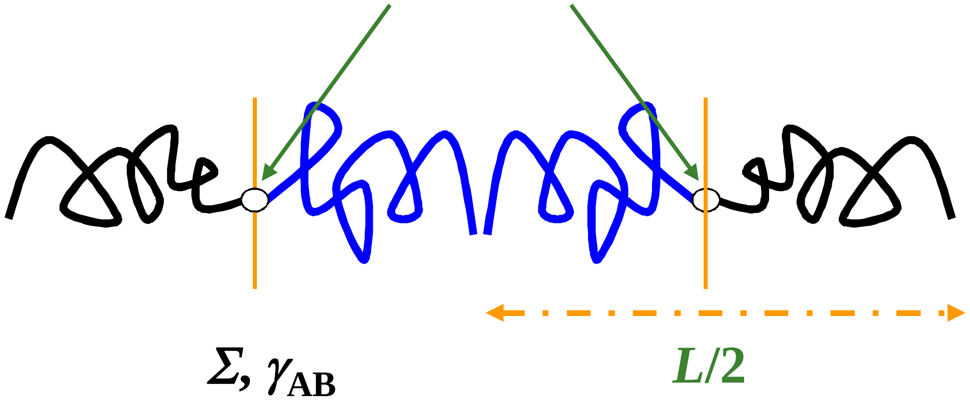
Microphase Separation of Triblock Copolymers



Thermodynamics of Microphase Separation



Lamellar structure



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

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

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

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

Thermodynamics of Microphase Separation

- **Free energy of lamellae:** $F_{LAM} = \underbrace{\gamma_{AB}\Sigma}_{\text{enthalpic term}} + \underbrace{\frac{3}{2}kT\frac{(L/2)^2}{Nb^2}}_{\text{entropic spring term}}$ **See Appendix**

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

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

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

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

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

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** $\boxed{\chi_c N = 2}$

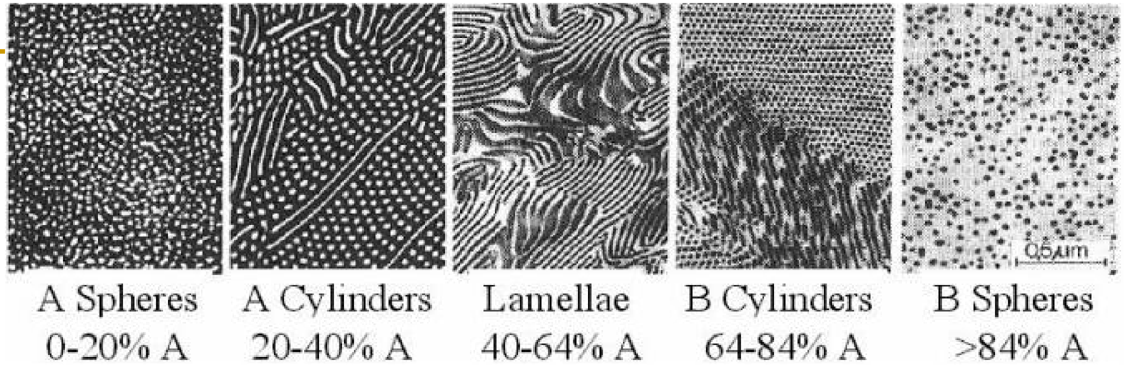
Appendix

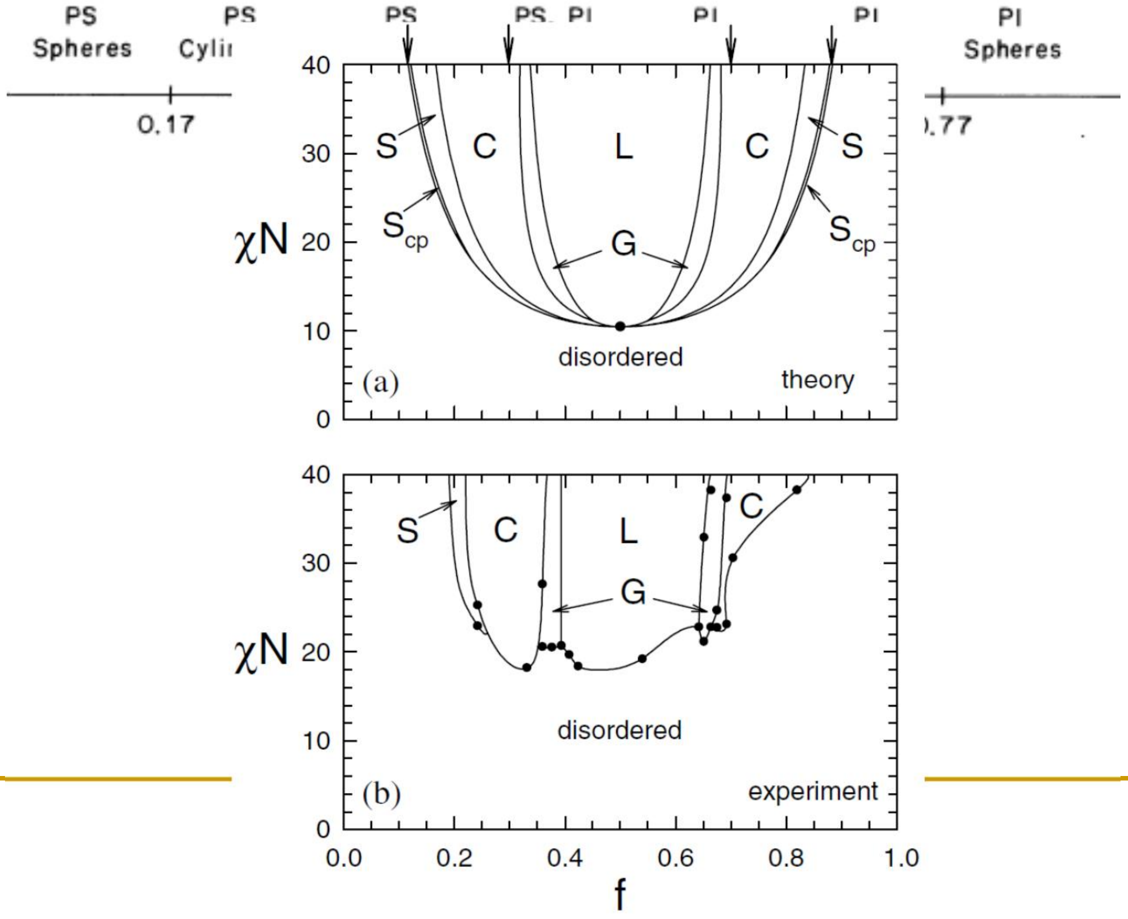
$$S_{el}(h) = k\ln\Omega = k\ln\Phi\left(h,N\right)\int\Phi\left(h,N\right)dh \approx k\ln\left[\left(\frac{3}{2\pi Nb^2}\right)^{3/2}\exp\left(-\frac{3h^2}{2Nb^2}\right)\right]$$

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

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

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


0.5µm
A Spheres
0-20% A
A Cylinders
20-40% A
Lamellae
40-64% A
B Cylinders
64-84% A
B Spheres
>84% A


PS
Spheres
PS
Cylii
PS
PS PI
PI
PI
PI
Spheres
0.17
).77
(a)
theory
S
C
L
C
S
S_cp
G
S_cp
disordered
χN
0
10
20
30
40
(b)
experiment
S
C
L
C
G
disordered
0.0
0.2
0.4
0.6
0.8
1.0
f

总结: 结构层次

链段(segment) $l_e = h_0^2/L$

热串滴 (Thermal Blob) $g_T \approx \left(\frac{u}{l^3}\right)^{-2}$ $\xi_T \approx \left(\frac{u}{l^3}\right)^{-1} l$ $\bar{E} \approx kTg_T^2 \frac{u}{\xi_T^3} \approx k_B T$

单链(Single Chain)和稀溶液 $h = N^{\nu} l_e$

亚浓溶液 从热串滴到大串滴(相关长度)再到链

浓溶液，θ溶液和熔体

嵌段共聚物

共混物 从自由能到化学势

高分子链构象的重要作用

高斯链模型代表构象熵的最大状态，高分子链总是要尽可能地实现这种构象熵的最大状态。溶液中链构象状态的实现概率要通过焓与构象熵最大化效应两者之间的竞争和平衡来决定。

χ参数的重要作用

(1) 溶液中链的构象(χ与构象熵的相互制约)

(2) 凝胶的体积相变(χ与混合熵、构象熵的相互制约)

(3) 高分子溶液和共混物的相平衡和相分离(χ与混合熵的相互制约)

(4) 高分子混合界面 (与χ有关的界面能与构象熵的相互制约)

~~(5) 高分子嵌段共聚物的微相分离 (与χ有关的界面能与构象熵的相互制约)~~

高分子溶液热力学 $\Delta G=\Delta H-T\Delta S$ $\quad \frac{\partial \Delta G}{\partial h}=0$ or $\Delta G=0$

焓　　排斥体积　　熵

高斯链：

$$H=0 \qquad \ln P(h)=0 \qquad S_{conf}=-\frac{3}{2}k_B\frac{\boldsymbol{h}^2}{xl^2}$$

稀溶液：

良溶剂，θ溶剂

$$H=-\frac{x^2v_c}{h^3}\chi \qquad \ln P(h)\approx-\frac{x^2v_c}{2h^3} \qquad S_{conf}=-\frac{3}{2}k_B\frac{\boldsymbol{h}^2}{xl^2}$$

不良溶剂

$$H/h^3\sim\left[-\frac{\chi}{v_c}\left(\frac{xv_c}{h^3}\right)^2+w\left(\frac{xv_v}{h^3}\right)^3\right]$$

构象熵可忽略 $\quad S_{conf}\approx 0$

三体相互作用

也可用标度理论+blob model处理

亚浓溶液： 两体＋三体相互作用　排斥体积部分屏蔽

$$S_{conf}=-\frac{3}{2}k_B\frac{\boldsymbol{h}^2}{xl^2}$$

只能用标度理论+blob model处理

焓　　　熵

聚电解质：

$$H_{electr}\left(R_e\right)\approx k_BT\frac{l_B\left(fN\right)^2}{R_e}$$ (圆球)

or

$$H_{electr}\left(R_e\right)\approx k_BT\frac{l_B\left(fN\right)^2}{R_e}\ln\left(\frac{R_e}{N^{1/2}b}\right)$$ (椭球)

$$S=-\frac{3}{2}k_B\frac{\boldsymbol{h}^2}{Nl^2}$$

良溶剂下χ相互作用可忽略　排斥体积作用可忽略

浓溶液：

$$\Delta H_M=k_BT\frac{V_m}{\bar{V}_s}\chi\phi_1\phi_2$$

排斥体积被屏蔽

$$\Delta S_M=-k_B\frac{V_m}{\bar{V}_s}\left(\frac{\phi_1}{x_1}\ln\phi_1+\frac{\phi_2}{x_2}\ln\phi_2\right)$$

$$\Delta S_{conf}=0$$

Flory-Huggins Theory

凝胶：

$$\Delta H_M=k_BT\frac{V_m}{\bar{V}_s}\chi\phi_1\phi_2$$

$$\Delta S=-k_B\frac{V_m}{\bar{V}_s}\left(\frac{\phi_1}{1}\ln\phi_1+\frac{\phi_2}{x}\ln\phi_2\right)-\frac{3}{2}N_0k_B\frac{\Delta\left(\boldsymbol{h}^2\right)}{h_0^2}$$

N_0:单位体积内的网链数目

高分子共混物和嵌段共聚物热力学

共混物：

$$\Delta H_M = k_B T \frac{V_m}{V_s} \chi \phi_1 \phi_2 \qquad \Delta S_M = -k_B \frac{V_m}{V_s}\left(\frac{\phi_1}{x_1}\ln\phi_1 + \frac{\phi_2}{x_2}\ln\phi_2\right) \qquad \Delta S_{conf} = 0$$

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

→ $\Delta\mu_{i,1} = \Delta\mu_{i,2} \quad i = 1, 2$ Phase equilibrium (binodal)

→ $\frac{\partial^2 \Delta G_M}{\partial \phi^2} = 0$ Phase stability (spinodal)

$\frac{\partial^3 \Delta G_M}{\partial \phi^3} = 0$ Critical Point

Phase Diagram

Symmetric Blends: $\chi_c N = 2$ Solutions: $\chi_c = 1/2$

对称的嵌段共聚物：

有序相： $\Delta H_{\text{interface}} = \gamma_{AB}\Sigma$ $\quad \Delta S_{conf} \approx -\frac{3}{2}kT\frac{(L/2)^2}{Na^2}$ $\quad \frac{\partial \Delta F}{\partial L} = 0$ ➡ L_{opt}

无序相： $\Delta H \approx \frac{\widetilde{V}_m}{\widetilde{V}_s}\chi_{AB}\phi_A\phi_B kT = N\chi_{AB}\phi_A\phi_B kT$ $\quad \Delta S_{conf} \approx 0$

相平衡： ➡ $\Delta F_{disoeder} = \Delta F_{order}$ ➡ Critical Point: $\chi_c N = 10.5$