

Polymers Physics

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Outline

1. **“Real” Chains**
2. Thermodynamics of Mixtures
3. Polymer Solutions

Summary of Ideal Chains

Ideal chains: no interactions between monomers separated by many bonds

Mean square end-to-end distance of ideal linear polymer $\langle R^2 \rangle = Nb^2$

Mean square radius of gyration of ideal linear polymer $\langle R_g^2 \rangle = \frac{Nb^2}{6}$

Probability distribution function $P_{3d}(N, \vec{R}) = \left(\frac{3}{2\pi Nb^2} \right)^{3/2} \exp\left(-\frac{3R^2}{2Nb^2} \right)$

Free energy of an ideal chain $F = \frac{3}{2} kT \frac{\vec{R}^2}{Nb^2}$

Entropic Hooke's Law $\vec{f} = \frac{3kT}{Nb^2} \vec{R}$

Pair correlation function $g(r) = \frac{3}{\pi} \frac{1}{rb^2}$

Real Chains

Include interactions between all monomers

Short-range (in space) interactions

Probability of a monomer to be in contact with another monomer for d -dimensional chain

$$\phi^* \approx b^d \frac{N}{R^d}$$

If chains are ideal $R \approx bN^{1/2}$ $\phi^* \approx N^{1-d/2}$ small for $d > 2$

Number of contacts between pairs of monomers that are far along the chain, but close in space $N\phi^* \approx N^{2-d/2}$ small for $d > 4$

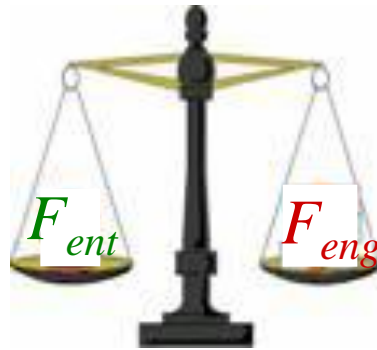
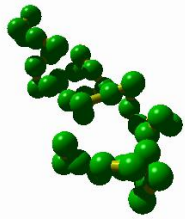
For $d < 4$ there are many contacts between monomers in an ideal chain.

Interactions between monomers change conformations of real chains.

Life of a Polymer is a Balance

of entropic and energetic parts of free energy

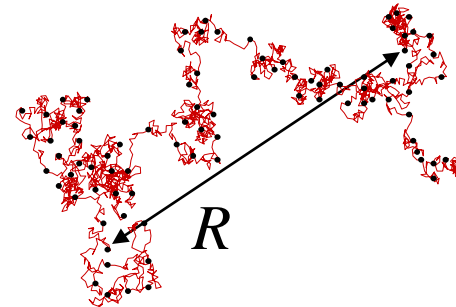
Entropic part “wants” chains to have ideal-like conformations



Energetic part typically “wants” something else (e.g. fewer monomer-monomer contacts in a good solvent).



Chain has to find a compromise between these two desires and optimize its shape and size.



Flory Theory



Number density of monomers in a chain is N/R^3

Probability of another monomer being within excluded volume ν of a given monomer is $\nu N/R^3$

Excluded volume interaction energy per monomer $kT\nu N/R^3$

Excluded volume interaction energy per chain $kT\nu N^2/R^3$

Entropic part of the free energy is of order $kTR^2/(Nb^2)$

Flory approximation of the total free energy of a real chain

$$F \approx kT \left(\nu \frac{N^2}{R^3} + \frac{R^2}{Nb^2} \right)$$

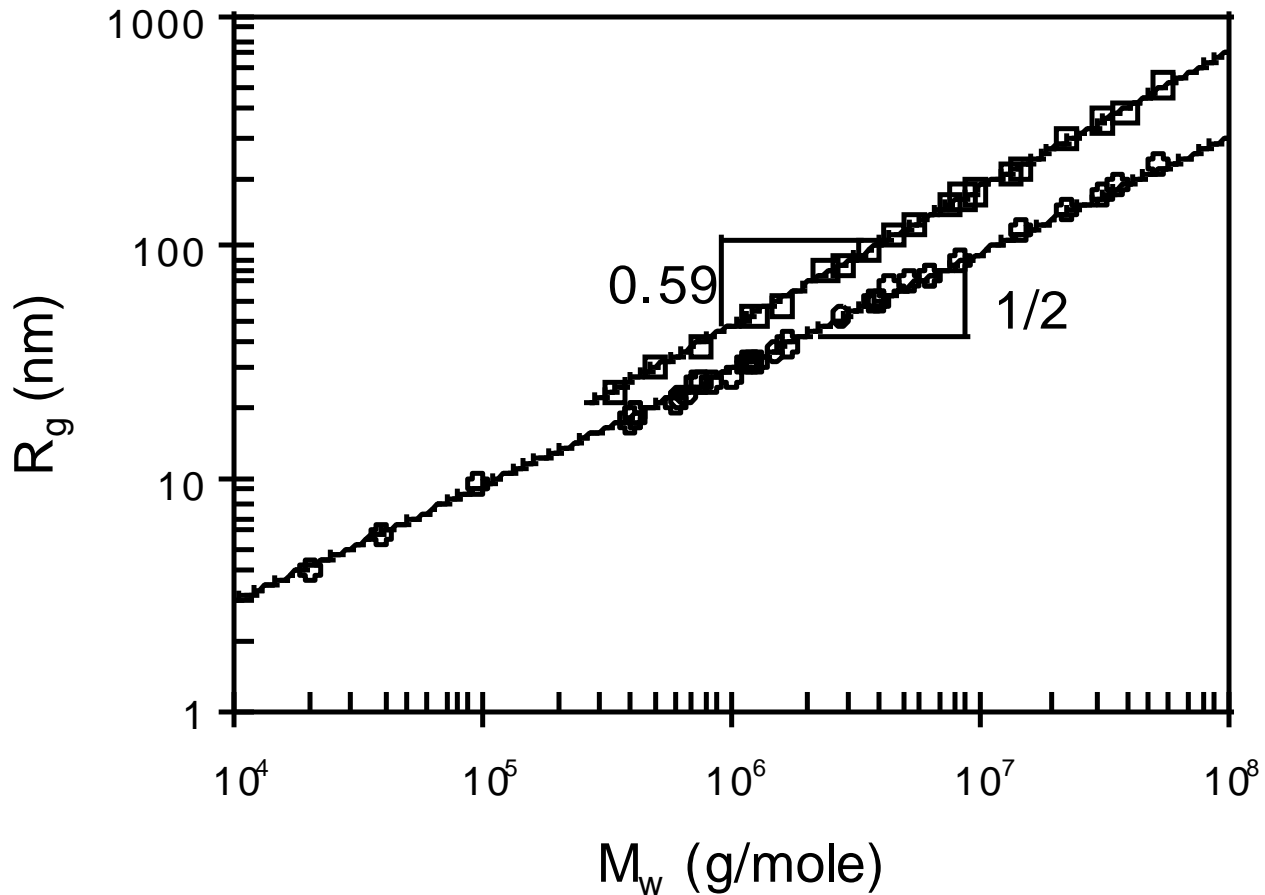
Free energy is minimum at $R \approx \nu^{1/5} b^{2/5} N^{3/5}$

Universal relation $R \sim N^\nu$

ν - Flory scaling exponent

More accurate estimate $\nu \cong 0.588$





Radius of gyration of polystyrene chains in a θ -solvent (cyclohexane at 34.5°C) and in a good solvent (benzene at 25°C).
Fetters et al *J. Phys. Chem. Ref. Data* **23**, 619 (1994)

Polymer Under Tension



Ideal chain

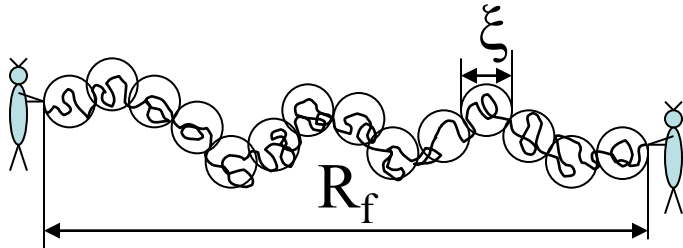
Real chain

Unperturbed size



$$R_0 \approx bN^{1/2}$$

$$R_F \approx bN^{3/5}$$



Tension blobs (Pincus blobs) of size ξ contain g monomers

Chains are almost unperturbed on length scales up to ξ

$$\xi \approx bg^{1/2}$$

$$\xi \approx bg^{3/5}$$

On larger length scales they are stretched arrays of Pincus blobs

$$R_f \approx \xi \frac{N}{g} \approx \frac{Nb^2}{\xi} \approx \frac{R_0^2}{\xi}$$

$$R_f \approx \xi \frac{N}{g} \approx \frac{Nb^{5/3}}{\xi^{2/3}} \approx \frac{R_F^{5/3}}{\xi^{2/3}}$$

Size of Pincus blobs

$$\xi \approx \frac{R_0^2}{R_f}$$

$$\xi \approx \frac{R_F^{5/2}}{R_f^{3/2}}$$

Polymer Under Tension

Ideal chain

$$\xi \approx \frac{R_0^2}{R_f}$$

Size of Pincus blobs

Real chain

$$\xi \approx \frac{R_F^{5/2}}{R_f^{3/2}}$$

Free energy cost for stretching a chain is on order kT per blob

$$F \approx kT \frac{N}{g} \approx kT \frac{R_f}{\xi} \approx kT \left(\frac{R_f}{R_0} \right)^2$$

$$F \approx kT \frac{N}{g} \approx kT \frac{R_f}{\xi} \approx kT \left(\frac{R_f}{R_F} \right)^{5/2}$$

Tension force is on order kT divided by blob size ξ

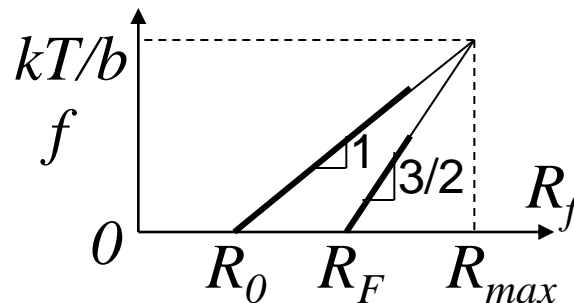
$$f \approx \frac{kT}{\xi} \approx \frac{kT}{R_0^2} R_f \approx \frac{kT}{R_0} \frac{R_f}{R_0}$$

$$f \approx \frac{kT}{\xi} \approx \frac{kT}{R_F^{5/2}} R_f^{3/2} \approx \frac{kT}{R_F} \left(\frac{R_f}{R_F} \right)^{3/2}$$

linear elasticity

For $b = 1nm$ at room T

$$kT/b = 4pN$$



non-linear elasticity

even at low forces

Log - log plot

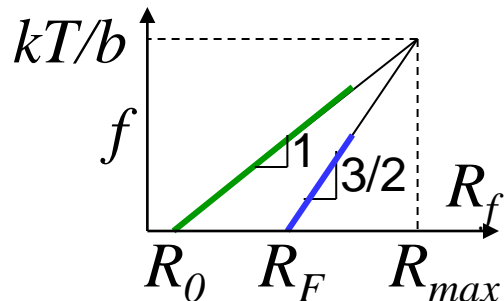


Polymer Under Tension

Ideal chain

$$f \approx \left(kT / R_0^2 \right) R_f$$

linear elasticity



Real chain

$$f \approx \left(kT / R_F^{5/2} \right) R_f^{3/2}$$

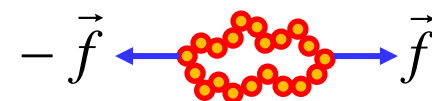
non-linear elasticity

Challenge Problem 1: Pulling a Ring



Consider a pair of forces applied to monomers 1 and $1+N/2$

i. Show that the modulus of an ideal ring is twice the modulus of a linear $N/2$ -mer



ii. How does modulus of a ring in a good solvent G_r compare to twice the modulus of linear $N/2$ -mer $G_{N/2}$?



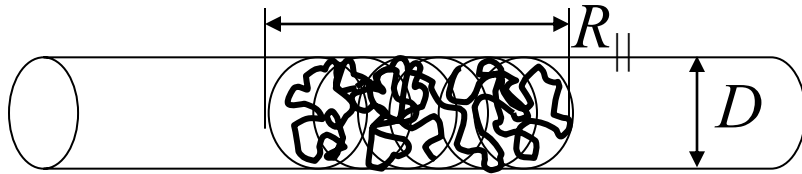
a. $G_r = 2G_{N/2}$ similar to ideal case

b. $G_r < 2G_{N/2}$ because the entropy of sections of a ring is lower

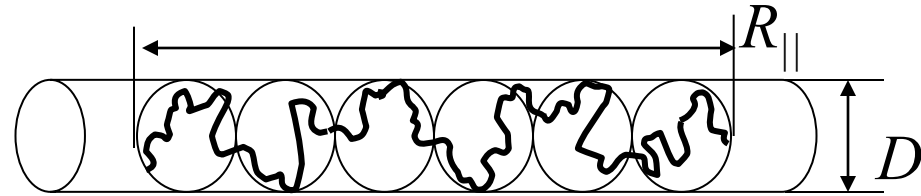
c. $G_r > 2G_{N/2}$ because ring sections reinforce each other

Biaxial Compression

Ideal chain



Real chain



On length scales smaller than compression blob of size D chain is almost unperturbed

$$g \approx \left(\frac{D}{b}\right)^2$$

$$g \approx \left(\frac{D}{b}\right)^{5/3}$$

Occupied part of the tube

$$R_{\parallel} \approx D \left(\frac{N}{g}\right)^{1/2} \approx bN^{1/2}$$

$$R_{\parallel} \approx D \left(\frac{N}{g}\right) \approx \left(\frac{b}{D}\right)^{2/3} Nb$$

Free energy of confinement

$$F_{conf} \approx kT \frac{N}{g} \approx kTN \left(\frac{b}{D}\right)^2$$

$$F_{conf} \approx kT \frac{N}{g} \approx kTN \left(\frac{b}{D}\right)^{5/3}$$

$$F_{conf} \approx kT \left(\frac{R_0}{D}\right)^2$$

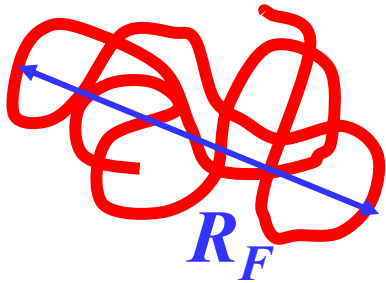
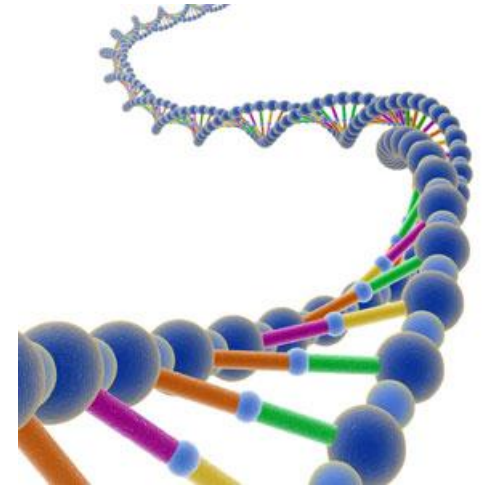
$$F_{conf} \approx kT \left(\frac{R_F}{D}\right)^{5/3}$$

Challenge Problem 2:

Biaxial Confinement of a Semiflexible Chain

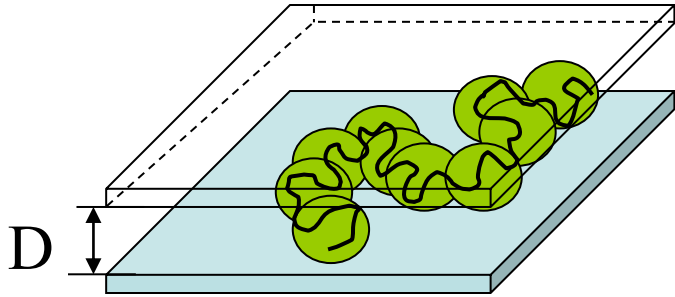
Consider a semiflexible polymer – e.g. double-stranded DNA with Kuhn length $b=100nm$ and contour length $L=16\mu m$.

Assume that excluded volume diameter of double helix is $d=3nm$ (larger than its actual diameter $2nm$ due to electrostatic repulsions).



Calculate the size R_F of this lambda phage DNA in dilute solution and the length $R_{||}$ occupied by this DNA in a cylindrical channel of diameter D (for $d < D < R_F$).

Uniaxial Compression



Free energy of confinement in a slit is the same as in the cylindrical pore

Longitudinal size of an ideal chain in a slit is the same as for an unperturbed ideal chain. $R_{\parallel} \approx bN^{1/2}$

2-dimensional Flory theory for real chain confined in a slit

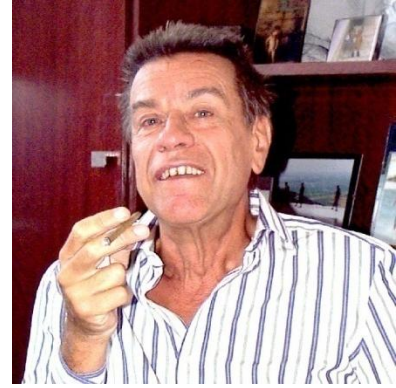
D^2 is the excluded area of a confinement blob with g monomers

$$F \approx kT \left(D^2 \frac{(N/g)^2}{R_{\parallel}^2} + \frac{R_{\parallel}^2}{(N/g)D^2} \right)$$

Longitudinal size of a real chain in a slit $R_{\parallel} \approx D \left(\frac{N}{g} \right)^{3/4} \approx bN^{3/4} \left(\frac{b}{D} \right)^{1/4}$

Fractal dimension of real chains in 2-d is $D = 4/3$

Scaling Model of Real Chains



Thermal blob - length scale at which excluded volume interactions are of order kT

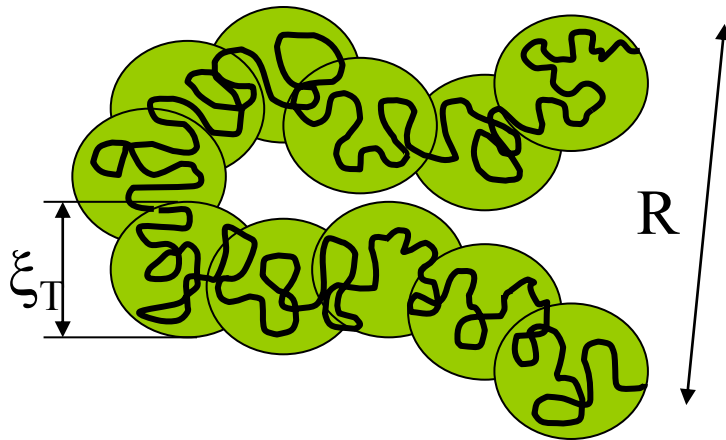
$$kT|v| \frac{g_T^2}{\xi_T^3} \approx kT$$

Chain is ideal on length scales smaller than thermal blob $\xi_T \approx b g_T^{1/2}$

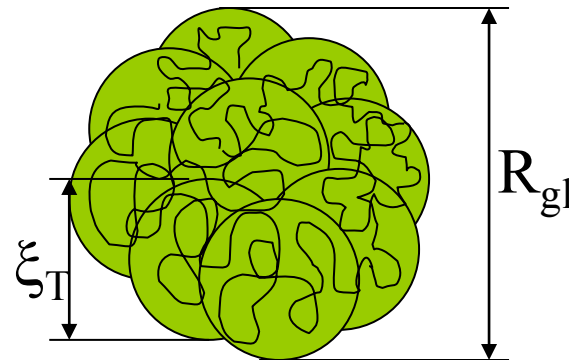
Number of monomers in a thermal blob $g_T \approx b^6/v^2$

Size of a thermal blob $\xi_T \approx \frac{b^4}{|v|}$

good solvent $v > 0$



poor solvent $v < 0$



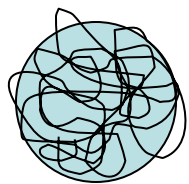
$$R \approx \xi_T \left(\frac{N}{g_T} \right)^{3/5} \approx b \left(\frac{v}{b^3} \right)^{1/5} N^{3/5}$$

$$R \approx \xi_T \left(\frac{N}{g_T} \right)^{1/3} \approx \frac{b^2}{|v|^{1/3}} N^{1/3}$$

Flory Theory of a Polymer in a Poor Solvent

$$F \approx kT \left(v \frac{N^2}{R^3} + \frac{R^2}{Nb^2} \right) \quad \text{In poor solvent } v < 0 \text{ and } R \rightarrow 0$$

Cost of Confinement



$$R < Nb^2$$

Compression blob of size R
with g monomers

$$g \approx \left(\frac{R}{b} \right)^2$$

Confinement free energy $F_{conf} \approx kT \frac{N}{g} \approx kT \frac{Nb^2}{R^2}$

$$F \approx kT \left(v \frac{N^2}{R^3} + \frac{R^2}{Nb^2} + \frac{Nb^2}{R^2} \right) \quad \text{For } v < 0 \quad R \rightarrow 0$$

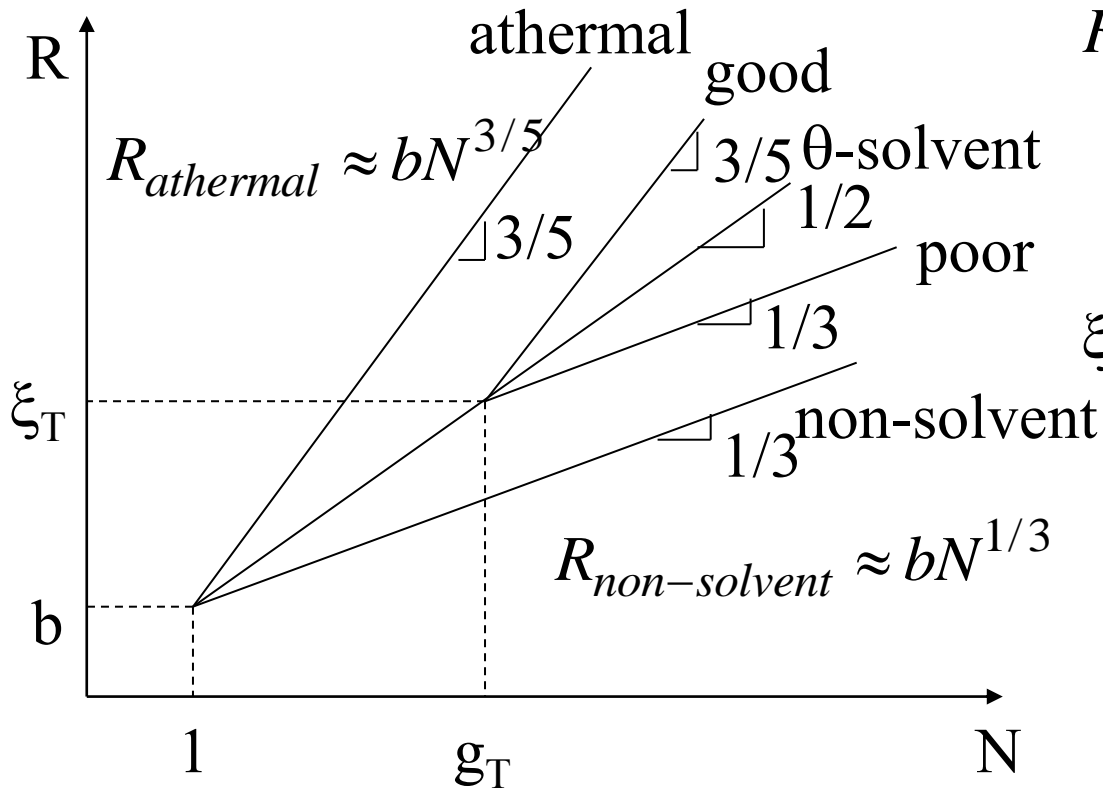
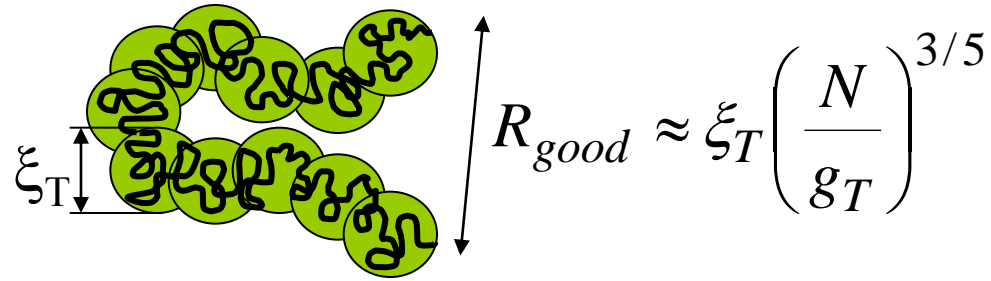
Three Body Repulsion

$$F \approx kT \left(\frac{R^2}{Nb^2} + \frac{Nb^2}{R^2} + v \frac{N^2}{R^3} + w \frac{N^3}{R^6} \right)$$

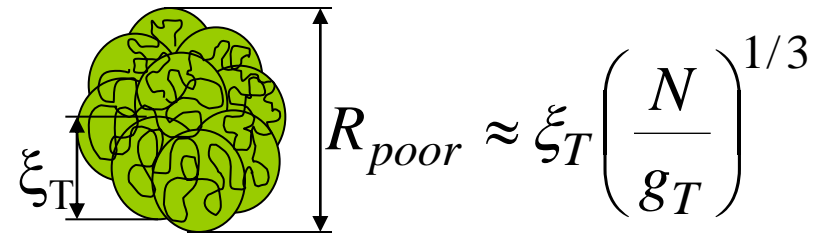
Size of a globule

$$R_{gl} \approx \left(\frac{wN}{|v|} \right)^{1/3}$$

Real Chains in Different Solvents



$R_\theta \approx bN^{1/2}$



Temperature Dependence of Chain Size

Mayer f -function

$$f(r) = \exp\left[-\frac{U(r)}{kT}\right] - 1 \approx \begin{cases} -1 & \text{for } r < b \text{ where } U(r) \gg kT \\ -\frac{U(r)}{kT} & \text{for } r > b \text{ where } |U(r)| < kT \end{cases}$$

Excluded volume

$$v \approx -4\pi \int_0^{\infty} f(r) r^2 dr \approx 4\pi \int_0^b r^2 dr + \frac{4\pi}{kT} \int_b^{\infty} U(r) r^2 dr \approx \left(1 - \frac{\theta}{T}\right) b^3$$

Interaction parameter z is related to number of thermal blobs per chain

$$z \approx \sqrt{\frac{N}{g_T}} \approx \frac{v}{b^3} N^{1/2} \approx \frac{T - \theta}{T} N^{1/2} \quad g_T \approx \frac{b^6}{v^2}$$

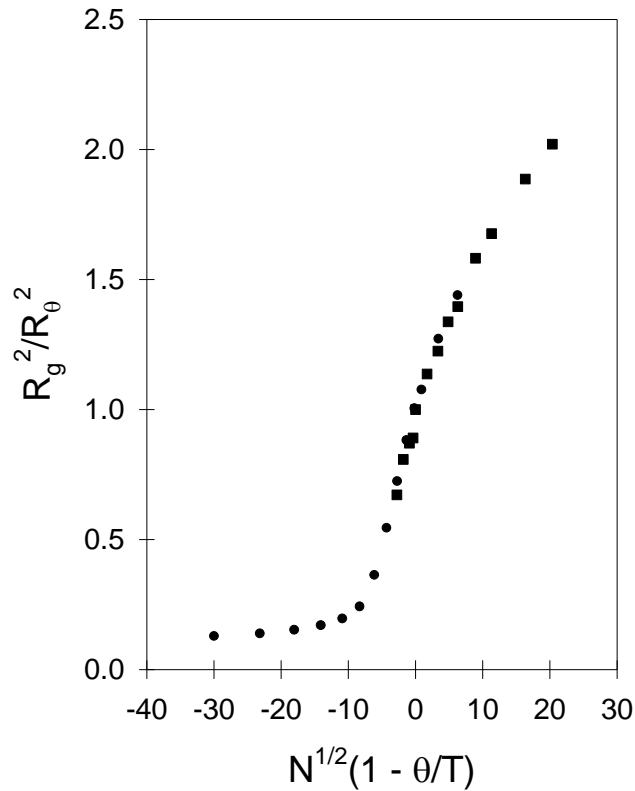
Chain contraction in a poor solvent

$$\frac{R}{bN^{1/2}} \approx |z|^{-1/3}$$

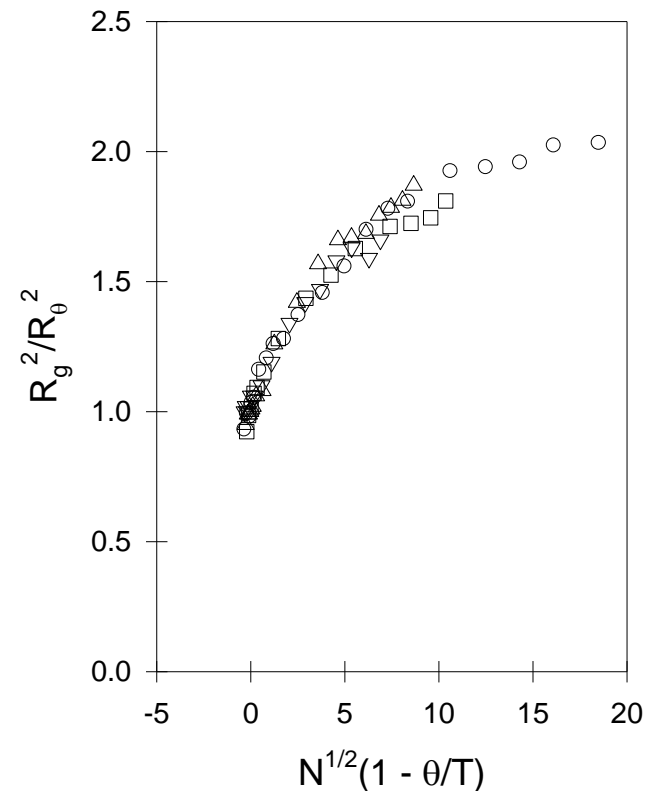
Chain swelling in a good solvent

$$\frac{R}{bN^{1/2}} \approx z^{2\nu-1}$$

Universal Temperature Dependence of Chain Size



Monte-Carlo simulations
Graessley et.al., *Macromolecules*
32, 3510, 1999 & I. Withers



Polystyrene in decalin
Berry, *J. Chem. Phys.*
44, 4550, 1966

Summary for Real Chains

Size of Linear Chains

Excluded volume

$R_\theta \approx bN^{1/2}$ nearly ideal in θ -solvents

$$v \approx b^3 \left(\frac{T - \theta}{T} \right)$$

$R_{good} \approx b \left(\frac{v}{b^3} \right)^{2\nu-1} N^\nu \approx b \left(\frac{v}{b^3} \right)^{0.18} N^{0.588}$ swollen in good solvents

$R_{athermal} \approx bN^\nu \approx bN^{0.588}$ in athermal solvents

$R_{poor} \approx |v|^{-1/3} b^2 N^{1/3}$ collapsed into a globule in poor solvents

In good solvents

Stretching a real chain

Confinement of a real chain

$$F \approx kT \left(\frac{R}{R_F} \right)^{1/(1-\nu)} \approx kT \left(\frac{R}{R_F} \right)^{2.43}$$

$$F \approx kT \left(\frac{R_F}{D} \right)^{1/\nu} \approx kT \left(\frac{R_F}{D} \right)^{1.7}$$

non-Hookean elasticity

Outline

1. Real Chains
2. **Thermodynamics of Mixtures**
3. Polymer Solutions

Binary Mixtures

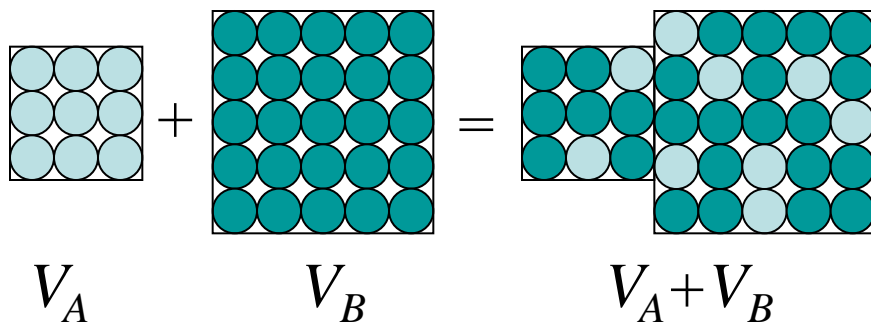
Homogeneous – if components are intermixed on a molecular scale

Heterogeneous – if there are distinct phases

Assume, for simplicity, **no volume change on mixing**

Consider a mixture with total number n of monomers (sites) and total volume $v_0 n$ where v_0 – volume of a lattice site

Assume that a monomer of each species occupies the same volume v_0

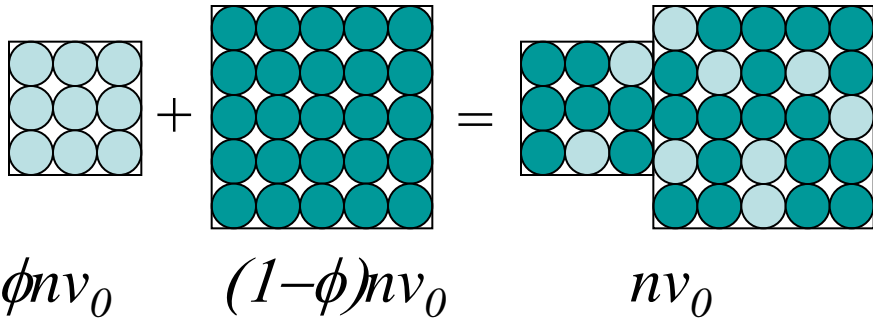


Volume fractions

$$\phi_A = \frac{V_A}{V_A + V_B} = \phi \quad \phi_B = 1 - \phi$$

$\phi_A n = \phi n$ monomers of type A and $\phi_B n_B = (1 - \phi)n$ monomers of type B

Entropy of Mixing



ϕ - volume fraction of A

$(1-\phi)$ - volume fraction of B

v_0 - volume of a lattice site

Number of translational states of a molecule in a mixture is the number of sites n

$$\Omega_{AB} = \frac{V_A + V_B}{v_0} = n$$

Number of states of molecule A in a pure A phase

$$\Omega_A = \frac{V_A}{v_0} = n\phi$$

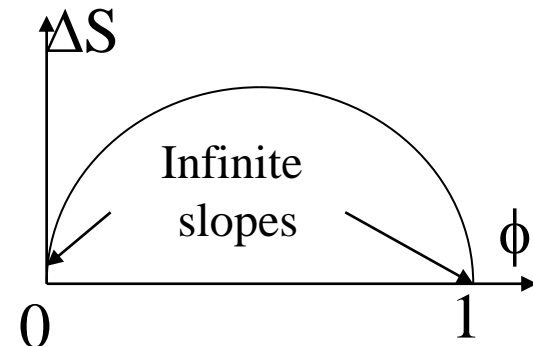
Entropy change upon mixing of a molecule A

$$\Delta S_A = k \ln \Omega_{AB} - k \ln \Omega_A = k \ln \left(\frac{\Omega_{AB}}{\Omega_A} \right) = k \ln \frac{1}{\phi} = -k \ln \phi$$

n_A/N_A and n_B/N_B - number of A and B molecules

Total entropy change upon mixing

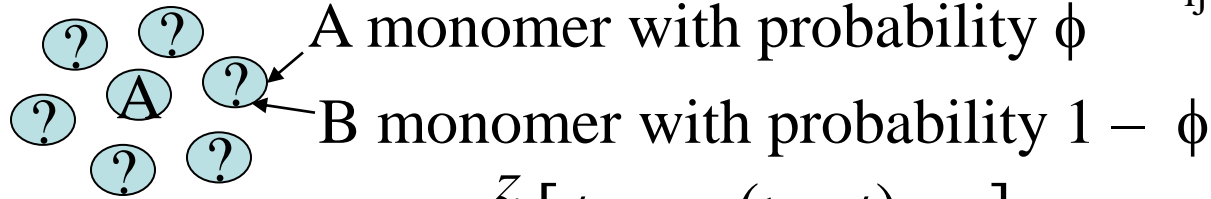
$$\Delta S = \frac{n_A}{N_A} \Delta S_A + \frac{n_B}{N_B} \Delta S_B = -k \left[\frac{n_A}{N_A} \ln \phi + \frac{n_B}{N_B} \ln(1-\phi) \right]$$



Energy of a Homogeneous Mixture

Mean Field Theory

Average energy per A monomer



$$u_A = \frac{z}{2} [\phi u_{AA} + (1 - \phi) u_{AB}]$$

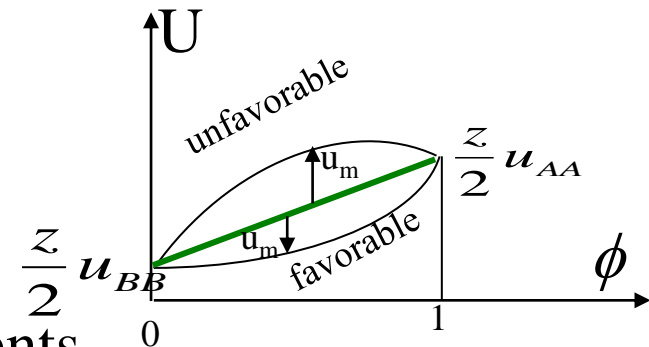
u_{ij} – interaction of i with j

z – coordination number
(number of neighbors)

Average energy per B monomer $u_B = \frac{z}{2} [\phi u_{AB} + (1 - \phi) u_{BB}]$

Average energy per monomer in homogeneous mixture

$$\begin{aligned} u_f &= \frac{n_A u_A + n_B u_B}{n} = \phi u_A + (1 - \phi) u_B = \\ &= \frac{z}{2} [\phi^2 u_{AA} + 2\phi(1 - \phi) u_{AB} + (1 - \phi)^2 u_{BB}] \end{aligned}$$



Average energy per monomer of pure components

before mixing $u_i = \frac{z}{2} [\phi u_{AA} + (1 - \phi) u_{BB}]$

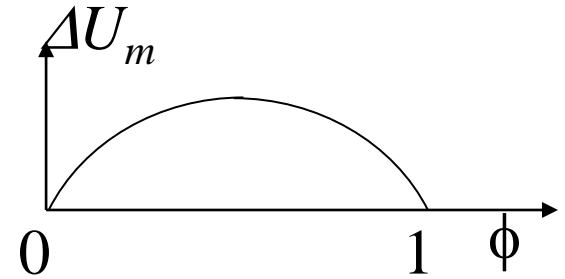
Energy of mixing $u_m = u_f - u_i$

Energy of Mixing

$$\Delta U_m = nu_m = n\phi(1-\phi)z \left[u_{AB} - \frac{u_{AA} + u_{BB}}{2} \right] = n\phi(1-\phi)kT\chi$$

Flory interaction parameter χ

$$\chi = \frac{z}{kT} \left[u_{AB} - \frac{u_{AA} + u_{BB}}{2} \right]$$



Probability of AB contact $\phi(1-\phi)$

Energy change on mixing per site $u_m = kT\chi\phi(1-\phi)$

Free Energy of Mixing

$$\Delta F_m = \Delta U_m - T\Delta S_m$$

per site
$$\frac{\Delta F_m}{n} = kT \left[\frac{\phi}{N_A} \ln \phi + \frac{(1-\phi)}{N_B} \ln(1-\phi) + \chi\phi(1-\phi) \right]$$

Regular solution: $N_A = N_B = 1$ Polymer solution: $N_A = N \gg 1, N_B = 1$

Polymer blend: $N_A \gg 1, N_B \gg 1$

Flory-Huggins Free Energy of Mixing

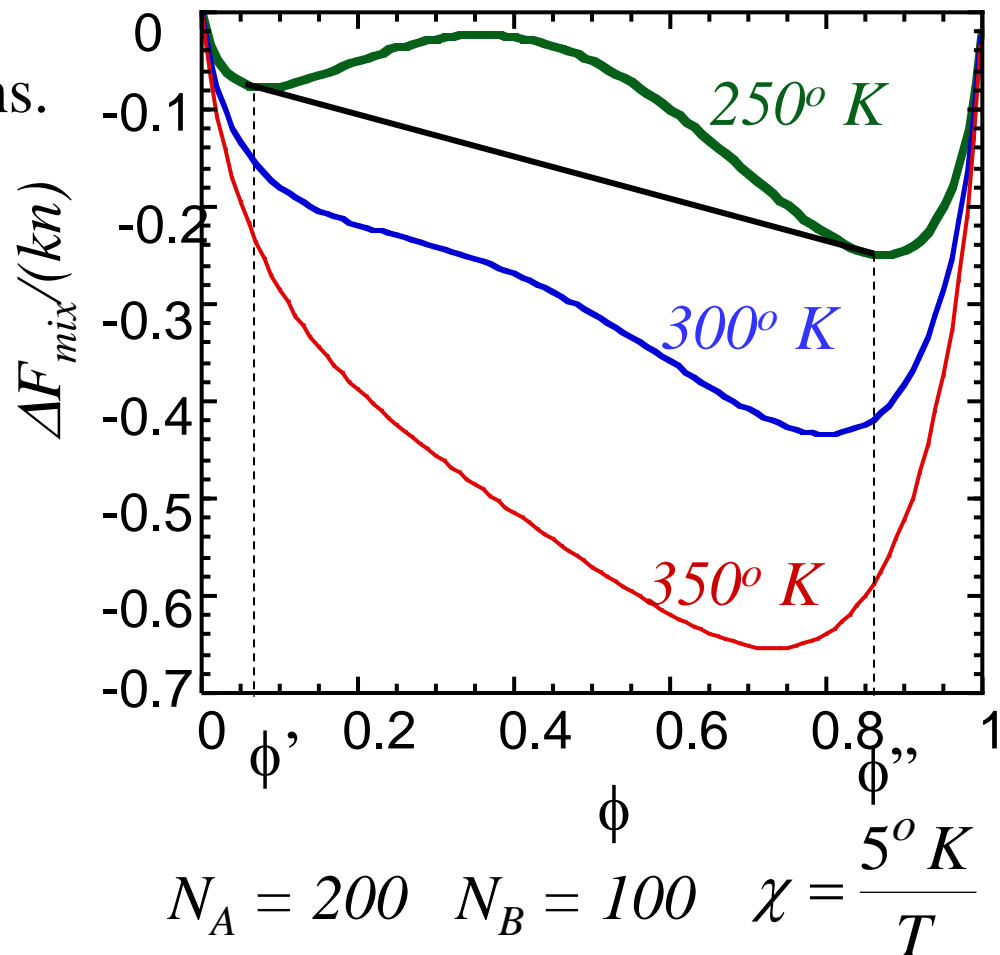
$$\frac{\Delta F_{mix}}{n} = kT \left(\frac{\phi}{N_A} \ln \phi + \frac{1-\phi}{N_B} \ln(1-\phi) + \chi \phi(1-\phi) \right)$$

At high T entropy of mixing dominates, ΔF_{mix} is convex and homogeneous mixture is stable at all compositions.

At lower T for $\chi > 0$ repulsive interactions are important and there is a composition range $\phi' < \phi < \phi''$

with thermodynamically stable phase separated state.

This composition range, called miscibility gap, is determined by the common tangent line.



Phase Diagrams

$$\frac{\Delta F_{mix}}{n} = kT \left(\frac{\phi}{N_A} \ln \phi + \frac{1-\phi}{N_B} \ln(1-\phi) + \chi \phi(1-\phi) \right)$$

For $\chi < \chi_{cr}$ mixture is stable at all compositions.

$$\text{For } \chi > \chi_{cr} = \frac{1}{2} \left(\frac{1}{\sqrt{N_A}} + \frac{1}{\sqrt{N_B}} \right)^2$$

there is a miscibility gap for $\phi' < \phi < \phi''$

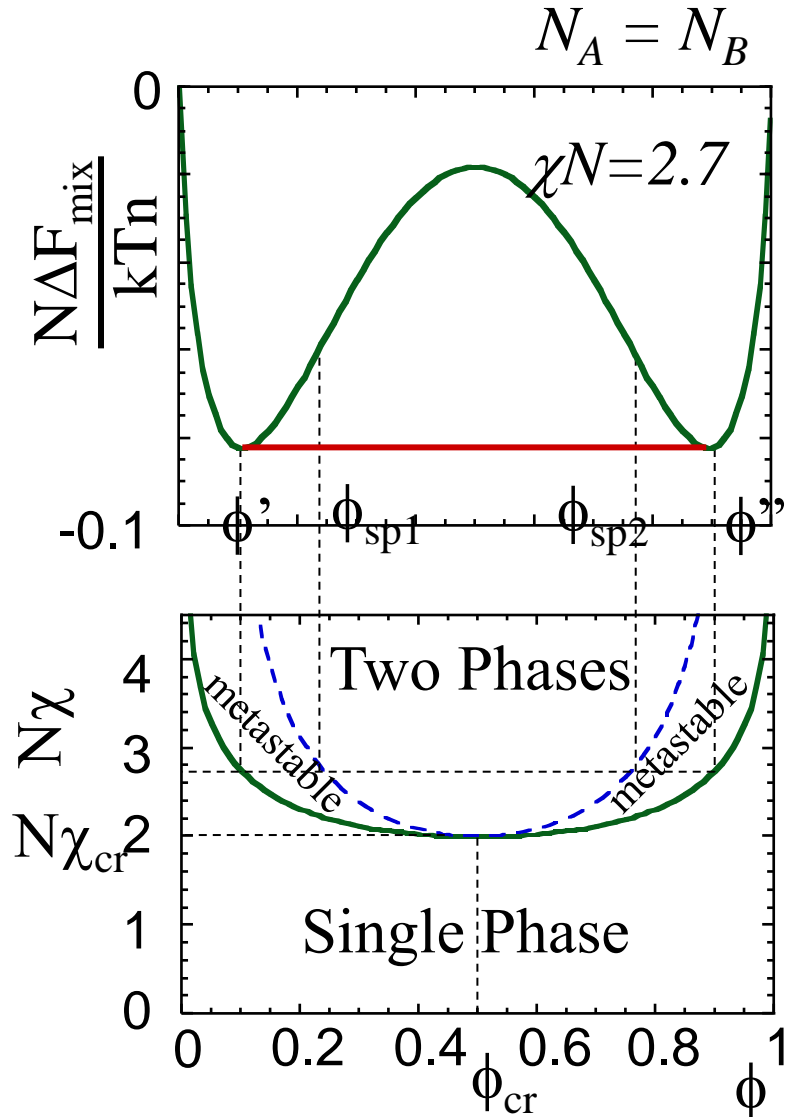
Critical composition
$$\phi_{cr} = \frac{\sqrt{N_B}}{\sqrt{N_A} + \sqrt{N_B}}$$

For a symmetric blend $N_A = N_B = N$

$$\chi_{cr} = 2/N \quad \phi_{cr} = 1/2$$

For polymer solutions $N_A = N, N_B = 1$

$$\chi_{cr} = \frac{1}{2} + \frac{1}{\sqrt{N}} + \frac{1}{2N} \quad \phi_{cr} \cong \frac{1}{\sqrt{N}}$$



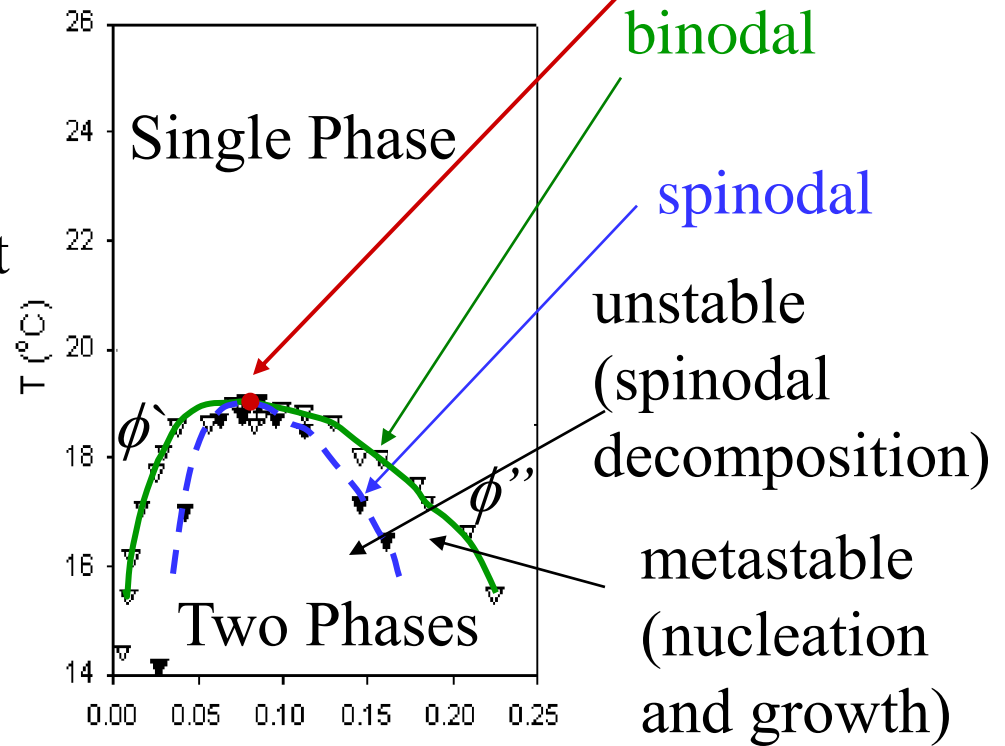
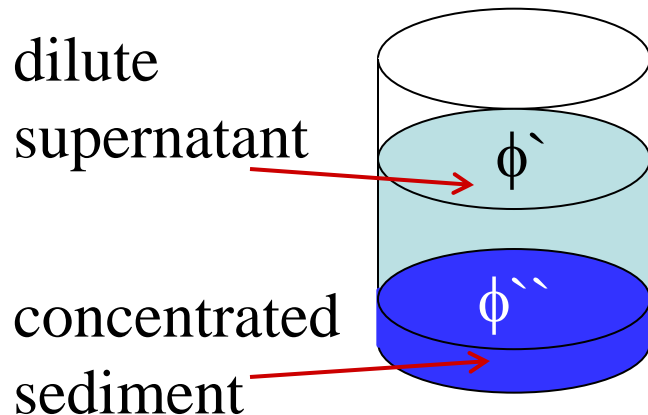
Phase Diagram of Polymer Solutions

Polymer solutions phase separate upon decreasing solvent quality below θ -temperature

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

Upper critical solution temperature $B > 0$

Solution phase separates below the binodal in poor solvent regime into a dilute supernatant of isolated globules at ϕ^* and concentrated sediment at ϕ^{**} .

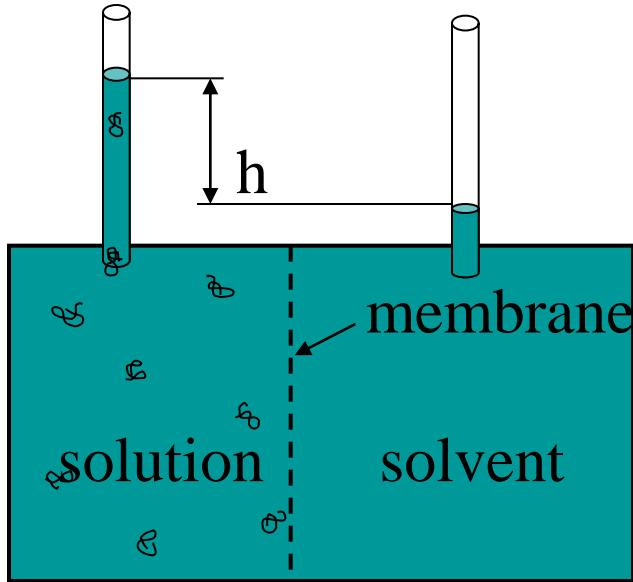


$M = 53.3 \text{ kg/mole}$

Polyisoprene in dioxane

Takano et al., Polym J. 17, 1123, 1985

Intermolecular Interactions



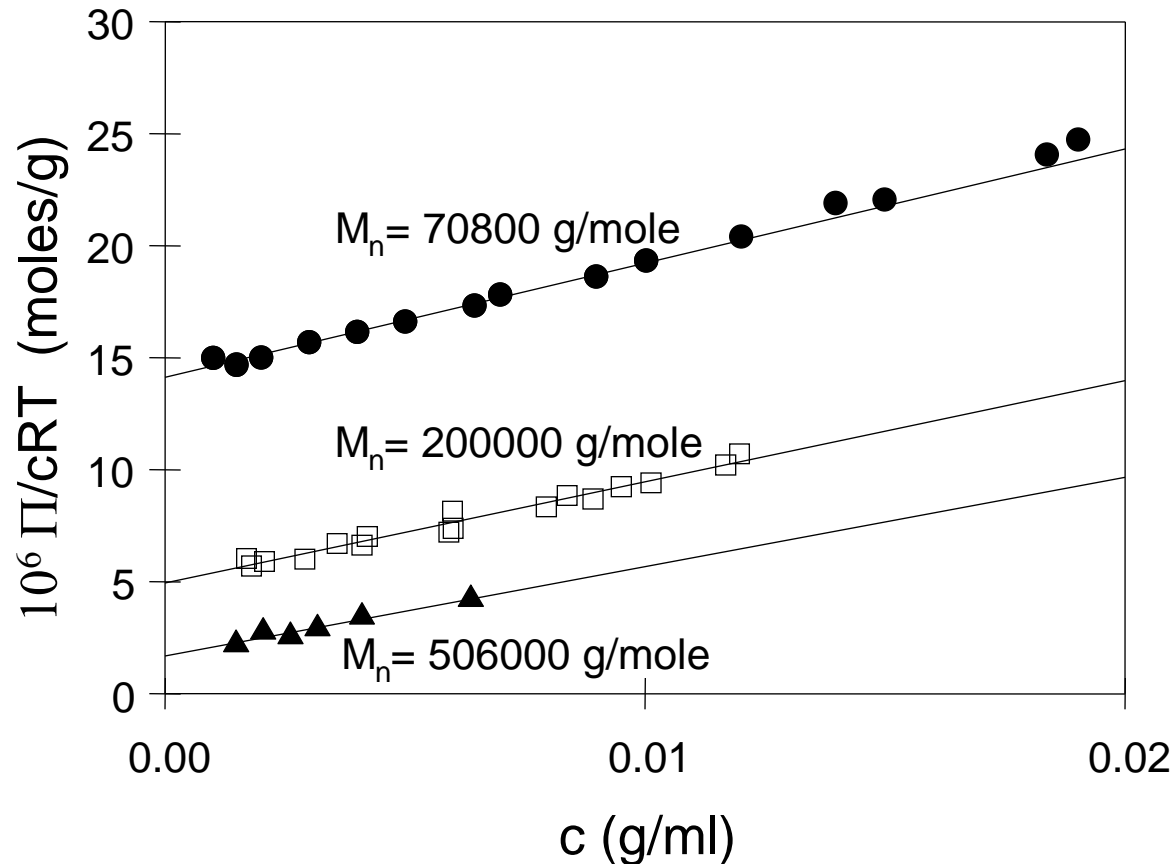
Osmometer

Poly(α -methylstyrene)
in toluene at 25 °C
Noda et al, Macromol.
16, 668, 1981

Osmotic pressure

$$\Pi = RT \left(\frac{c}{M_n} + A_2 c^2 + \dots \right)$$

A_2 – second virial coefficient



Mixtures at Low Compositions

$$\frac{\Delta F_{mix}}{n} = kT \left(\frac{\phi}{N_A} \ln \phi + \frac{1-\phi}{N_B} \ln(1-\phi) + \chi \phi(1-\phi) \right)$$

Expand $\ln(1-\phi)$ in powers of composition ϕ

$$\frac{\Delta F_{mix}}{n} \cong kT \left(\frac{\phi}{N_A} \ln \phi + \phi \left(\chi - \frac{1}{N_B} \right) + \frac{\phi^2}{2} \left(\frac{1}{N_B} - 2\chi \right) + \frac{\phi^3}{6N_B} + \dots \right)$$

Osmotic pressure

$$\Pi \equiv - \left. \frac{\partial \Delta F_{mix}}{\partial V} \right|_{n_A} = \frac{\phi^2}{b^3} \frac{\partial \left(\frac{\Delta F_{mix}}{n\phi} \right)}{\partial \phi} = \frac{kT}{b^3} \left(\frac{\phi}{N_A} + \left(\frac{1}{N_B} - 2\chi \right) \frac{\phi^2}{2} + \frac{\phi^3}{3N_B} + \dots \right)$$

Virial expansion in powers
of number density $c_n = \phi/b^3$

$$\Pi = kT \left(\frac{c_n}{N_A} + \frac{v}{2} c_n^2 + w c_n^3 + \dots \right)$$

Excluded volume $v = \left(\frac{1}{N_B} - 2\chi \right) b^3$ 3-body interaction $w = \frac{b^6}{3N_B}$

In polymer solutions $N_B = 1$ $\frac{v}{b^3} = 1 - 2\chi = \frac{T - \theta}{T} = \frac{2A_2 M_0^2}{b^3 N_{Av}}$

Polymer Melts

Consider a blend with a small concentration of N_A chains in a melt of chemically identical N_B chains.

No energetic contribution to mixing $\chi = 0$.

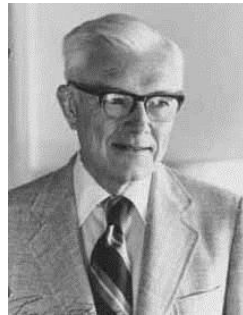
Excluded volume $v = \left(\frac{1}{N_B} - 2\chi \right) b^3 = \frac{b^3}{N_B}$ is very small for $N_B \gg 1$

Flory Theorem

Thermal blob $g_T \approx \frac{b^6}{v^2} = N_B^2$ $\xi_T \approx b\sqrt{g_T} \approx bN_B$

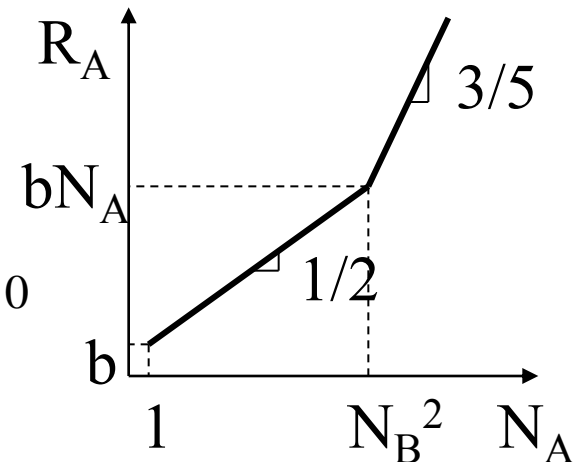
Chains smaller than thermal blob $N_A < N_B^2$ are nearly ideal.

In monodisperse $N_A = N_B$ and weakly polydisperse melts chains are almost **ideal**.



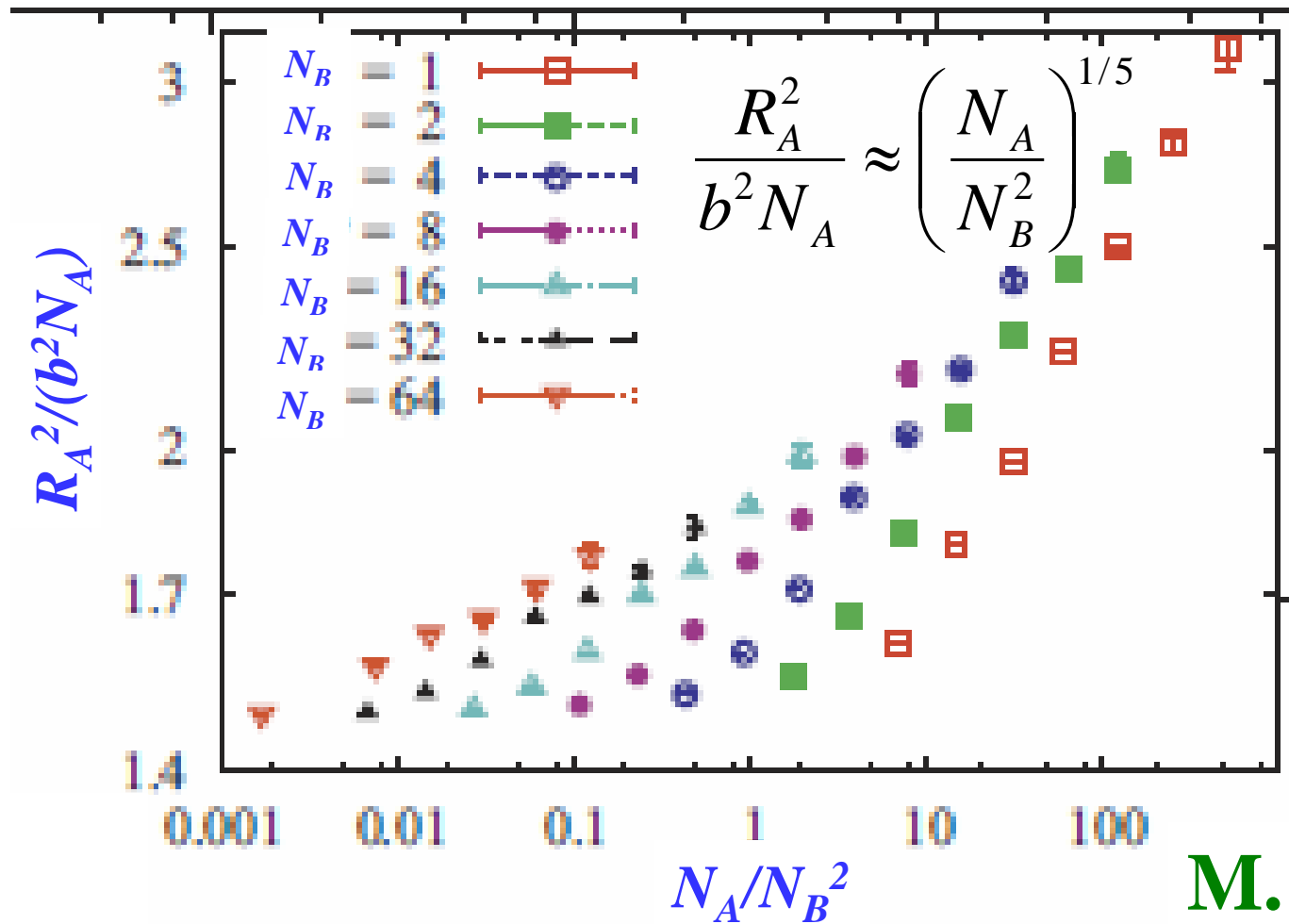
In strongly asymmetric blends $N_A > N_B^2$ long chains are swollen

$$R_A \approx \xi_T \left(\frac{N_A}{g_T} \right)^{3/5} \approx bN_B \left(\frac{N_A}{N_B^2} \right)^{3/5} \approx bN_A^{1/2} \left(\frac{N_A}{N_B^2} \right)^{1/10}$$



Challenge Problem 3:

Long N_A -mer in a 3-d Melt of N_B -mers

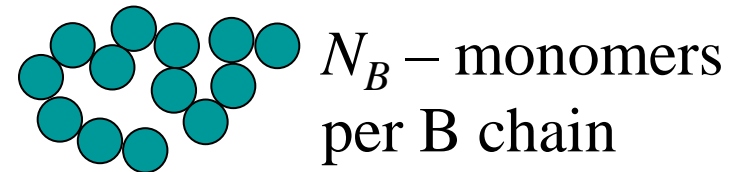
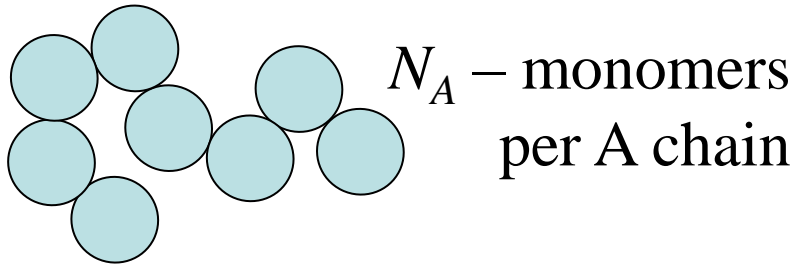


M. Lang

Why doesn't Flory Theorem work?

Challenge Problem 4:

Mixing of Polymers with Asymmetric Monomers

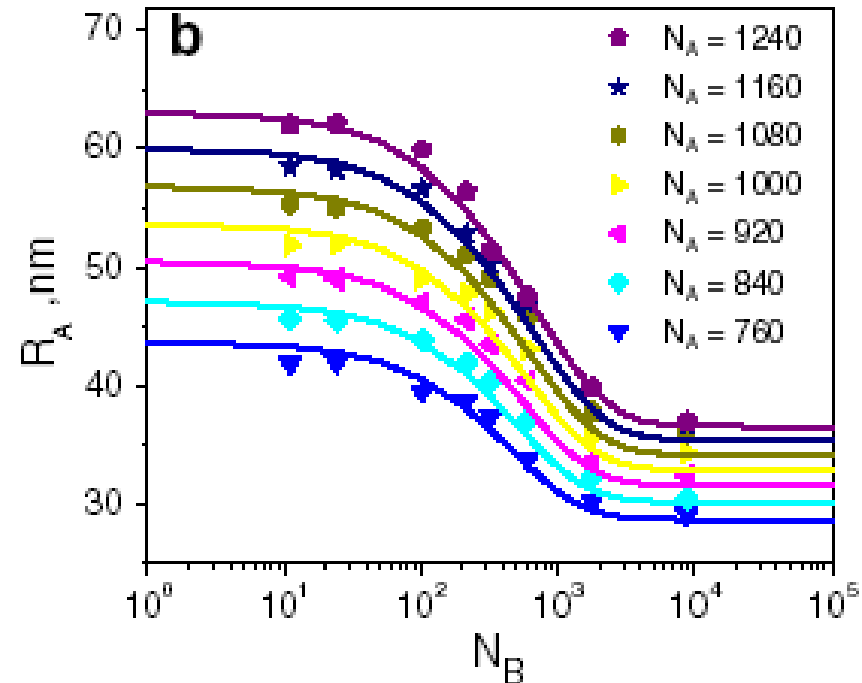


v_0 – volume of a lattice site = volume of a small B monomer

mv_0 – volume of an A monomer m times larger than B monomer

Derive the free energy of mixing ΔF_{mix} of A and B polymers.

Calculate the size R_A of dilute A-chains in a 2-d of B-chains for $m \gg 1$ in the case of $\chi=0$.



Summary of Thermodynamics of Mixtures

Free energy of mixing consists of entropic and energetic parts.

Entropic part per unit volume (translational entropy of mixing ΔS_{mix})

$$-\frac{T\Delta S_{mix}}{V} = kT \left[\frac{\phi}{v_A} \ln \phi + \frac{1-\phi}{v_B} \ln(1-\phi) \right]$$

Energetic part per unit volume

v_A – volume of A chain

v_B – volume of B chain

$$\frac{\Delta U_{mix}}{V} = kT \frac{\chi}{v_0} \phi(1-\phi)$$

v_0 – volume of a lattice site

Flory interaction parameter $\chi = A + \frac{B}{T}$

Many low molecular weight liquids are miscible

Some polymer – solvent pairs are miscible

Very few polymer blends are miscible

Chains are almost ideal in polymer melts as long as they are shorter than square of the average degree of polymerization $N_A < N^2$

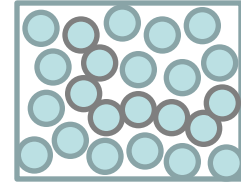
Outline

1. Real Chains
2. Thermodynamics of Mixtures
3. **Polymer Solutions**

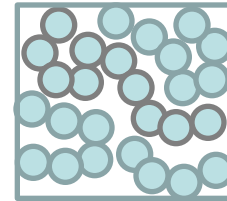
Quiz #1

Which of These Chains are Ideal?

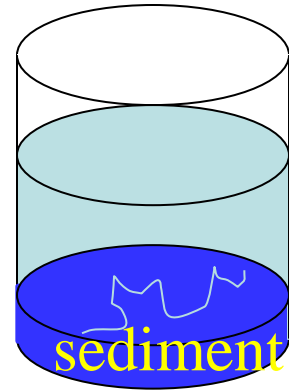
A. Polymer in a solution of its monomers



B. Polymer dissolved in a melt of identical chains



C. Chain in a sediment of a polymer solution
in a poor solvent



D. None of the above

Polymer Solutions

Theta solvent

$$v = (1 - 2\chi)b^3 = \frac{T - \theta}{T} b^3 = 0$$

Chains are nearly ideal at all concentrations $R = b\sqrt{N}$

Overlap concentration

$$\phi_{\theta}^* \approx \frac{Nb^3}{R^3} = \frac{1}{\sqrt{N}}$$

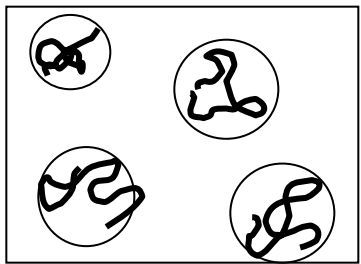
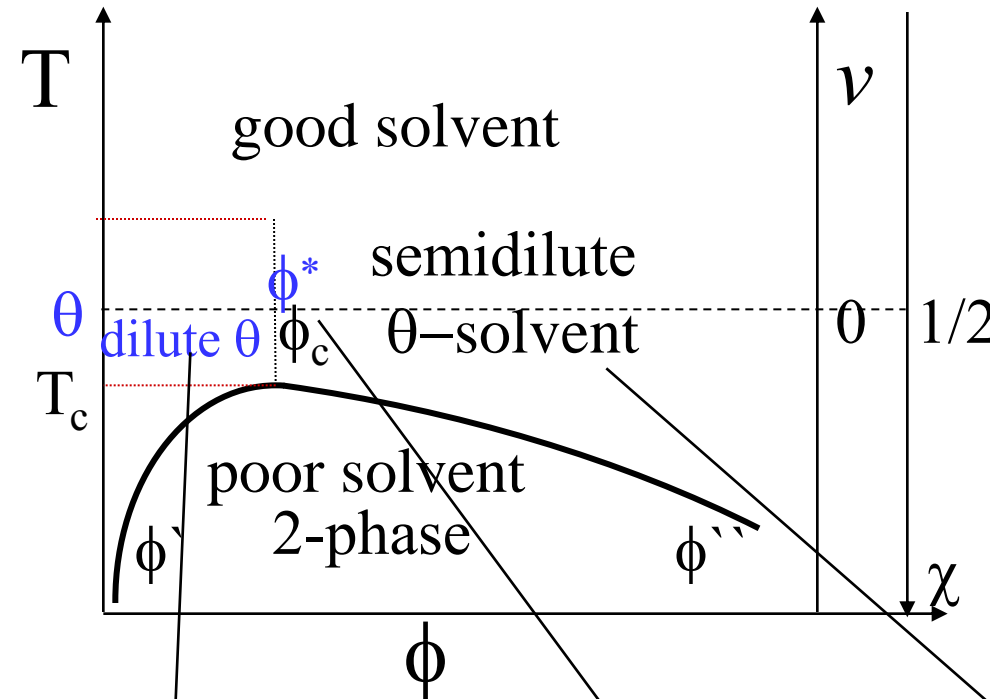
Chain is ideal if it is smaller than thermal blob $\xi_T \approx \frac{b^4}{|v|}$

Boundaries of dilute θ -regime

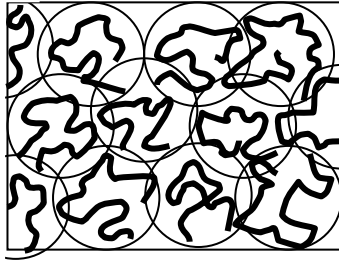
$$|v| = |1 - 2\chi|b^3 = \left| \frac{T - \theta}{T} \right| b^3 = \frac{b^3}{\sqrt{N}}$$

Temperatures at which chains begin to either swell or collapse

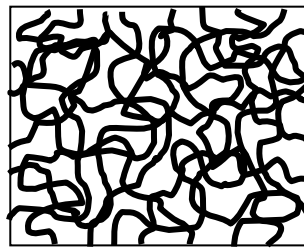
$$T \approx \theta \left(1 \pm \frac{1}{\sqrt{N}} \right)$$



$$\phi < \phi^*$$



$$\phi = \phi^*$$



$$\phi^* < \phi \ll 1$$

Poor Solvent

Critical composition $\phi_{cr} \approx \frac{1}{\sqrt{N}}$

Critical interaction parameter

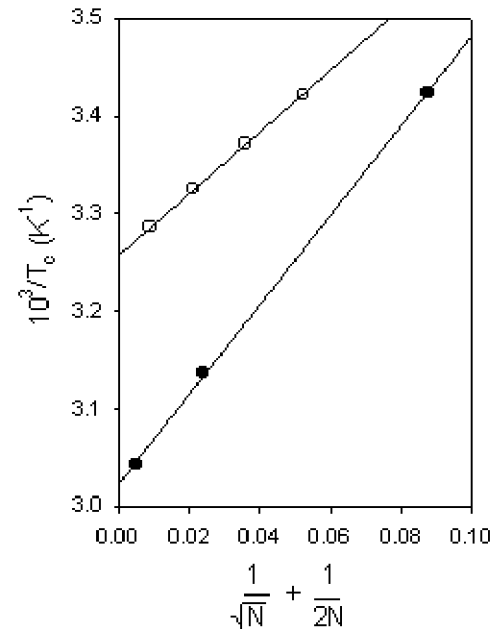
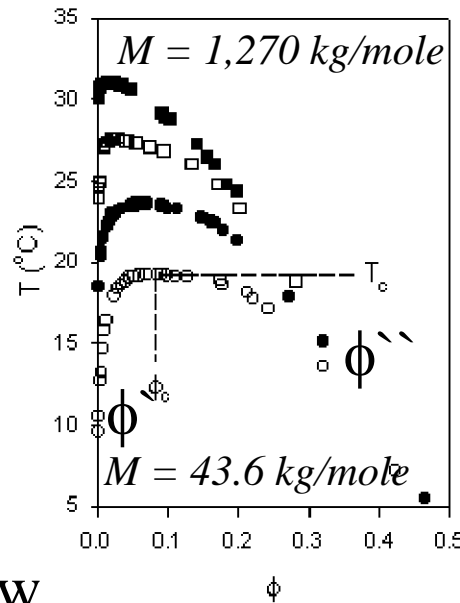
$$\chi_{cr} = \frac{1}{2} + \frac{1}{\sqrt{N}} + \frac{1}{2N}$$

Solution phase separates below the binodal into a dilute supernatant of isolated globules at ϕ^* and concentrated sediment at ϕ^{**} .

Sediment concentration ϕ^{**} is determined by the balance of second and third virial term (similar to the concentration inside globules).

$$\phi^{**} \approx -\frac{v}{b^3} \approx 2\chi - 1 \approx \frac{Nb^3}{R_{gl}^3}$$

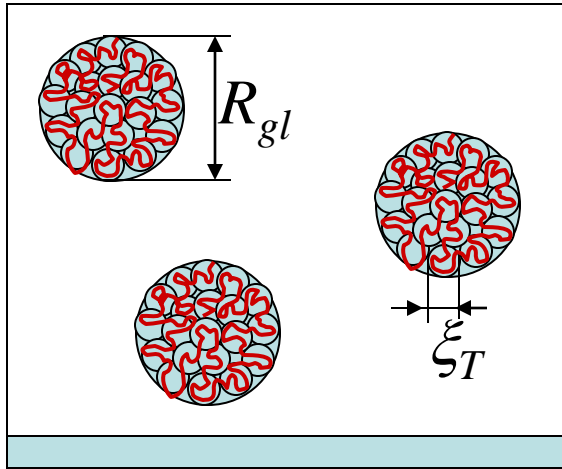
$$R_{gl} \approx \frac{bN^{1/3}}{(2\chi - 1)^{1/3}} \approx \frac{b^2 N^{1/3}}{|v|^{1/3}}$$



Polystyrene in cyclohexane (○) and polyisobutylene in diisobutyl ketone (●)
Shultz and Flory, J. Am. Chem. Soc. **74**, 4760, 1952

Poor Solvent

Dilute Supernatant of Globules



Globules behave as liquid droplets with size

$$R_{gl} \approx \frac{b^2 N^{1/3}}{|v|^{1/3}} \quad \xi_T \approx \frac{b^4}{|v|}$$

Surface tension is of order kT per thermal blob

$$\gamma \approx \frac{kT}{\xi_T^2} \approx \frac{kT}{b^8} v^2 \approx \frac{kT}{b^2} (2\chi - 1)^2$$

Total surface energy of a globule $\gamma R_{gl}^2 \approx \frac{kT R_{gl}^2}{\xi_T^2} \approx \frac{kT |v|^{4/3}}{b^4} N^{2/3}$
 is balanced by its translational entropy $kT \ln \phi'$

Concentration of a dilute supernatant

$$\phi' = \phi'' \exp\left(-\frac{\gamma R_{gl}^2}{kT}\right) \approx \frac{|v|}{b^3} \exp\left(-\frac{|v|^{4/3}}{b^4} N^{2/3}\right) \quad \text{is different from the mean field prediction.}$$

Good Solvent

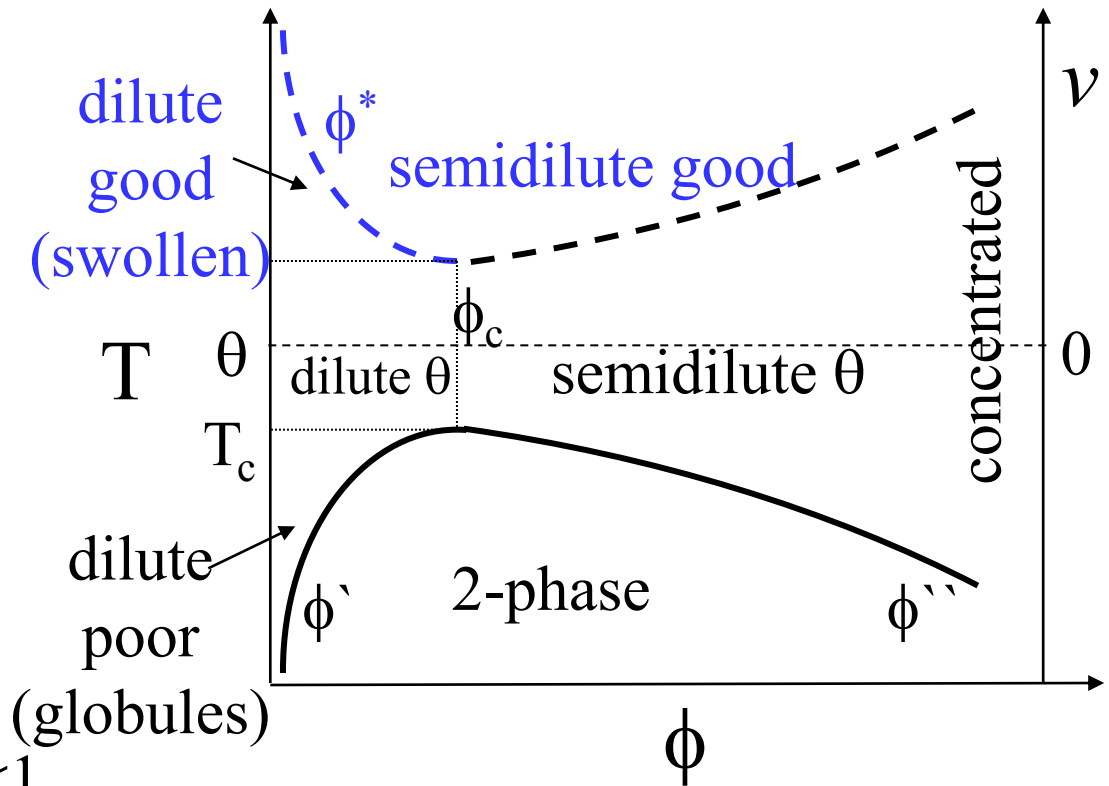
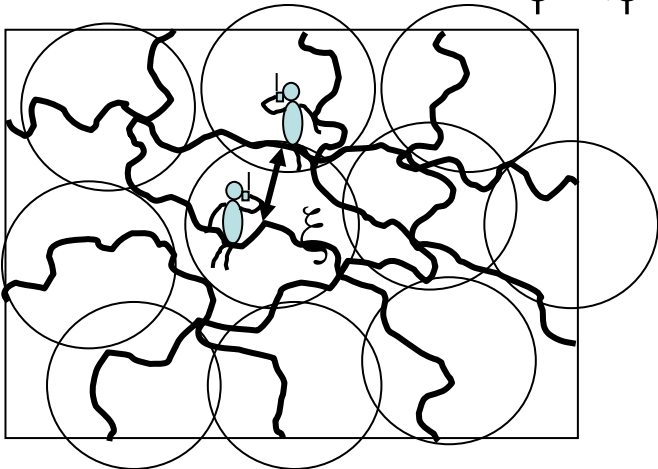
Swollen chain size
in dilute solutions

$$R \approx b \left(\frac{v}{b^3} \right)^{1/5} N^{3/5}$$

Overlap concentration

$$\phi^* \approx \frac{Nb^3}{R^3} \approx \left(\frac{b^3}{v} \right)^{3/5} N^{-4/5}$$

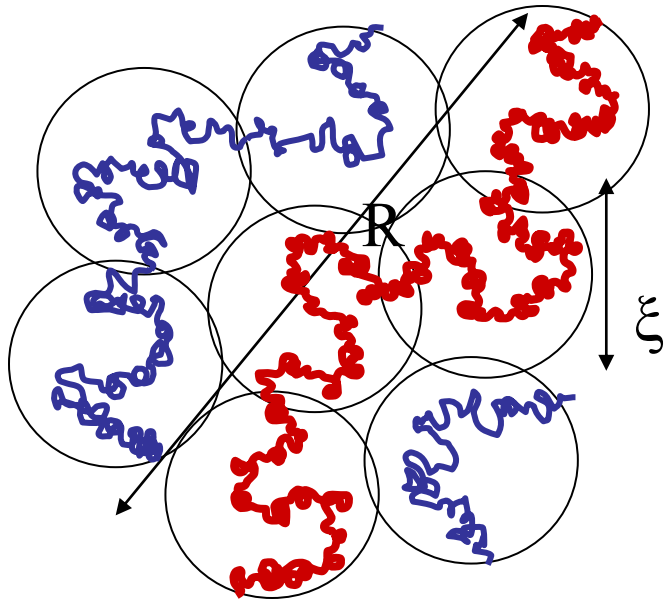
Semidilute solutions $\phi^* < \phi \ll 1$



Correlation length ξ

Distance from a monomer to nearest monomers on neighboring chains.

Correlation Length



For $r < \xi$ monomers are surrounded by solvent and monomers from the same chain.

The properties of this section of the chain of size ξ are the same as in dilute solutions.

$$\xi \approx b \left(\frac{v}{b^3} \right)^{1/5} g^{3/5}$$

g – number of monomers inside a correlation volume, called correlation blob.

Correlation blobs are at overlap $\phi \approx \frac{gb^3}{\xi^3}$

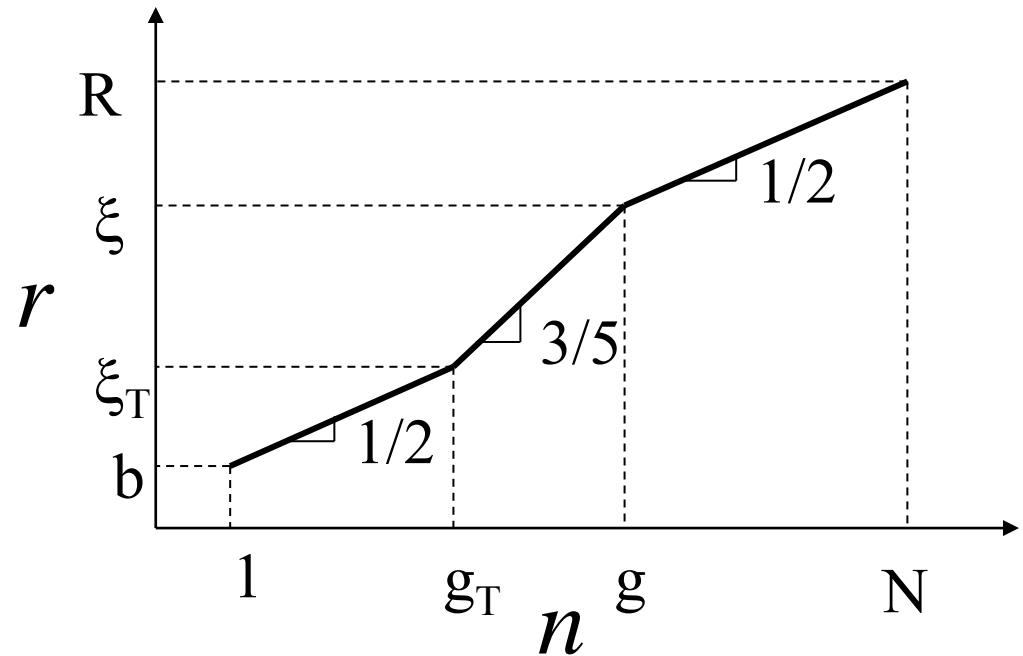
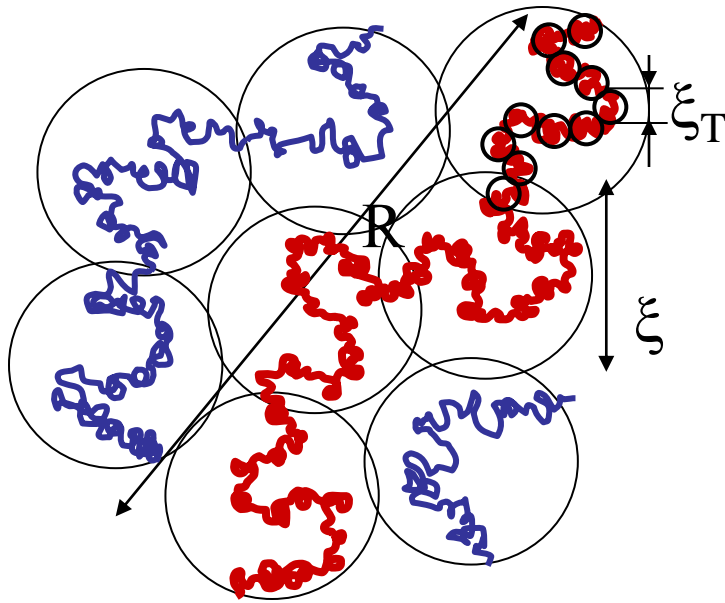
$$\xi \approx b \left(\frac{b^3}{v} \right)^{1/4} \phi^{-3/4}$$

For $r > \xi$ sections of neighboring chains overlap and screen each other.

On length scales $r > \xi$ polymers are ideal chains - melt with N/g effective segments of size ξ .

$$R \approx \xi \left(\frac{N}{g} \right)^{1/2} \approx b \left(\frac{v}{b^3 \phi} \right)^{1/8} N^{1/2}$$

Semidilute Solutions



On length scales less than ξ_T chain is ideal because excluded volume interactions are weaker than kT . $r \sim n^{1/2}$

On length scales larger than ξ_T but smaller than ξ excluded volume interactions are strong enough to swell the chain. $r \sim n^{3/5}$

On length scales larger than ξ excluded volume interactions are screened by surrounding chains. $r \sim n^{1/2}$

Scaling Theory of Semidilute Solutions

At overlap concentration $\phi^* \approx \left(\frac{b^3}{v}\right)^{3/5} N^{-4/5}$

chain has its dilute solution size $R_F \approx b\left(\frac{v}{b^3}\right)^{1/5} N^{3/5}$

In semidilute solutions R is a power of ϕ that matches dilute size at ϕ^*

$$R \approx R_F \left(\frac{\phi}{\phi^*}\right)^x \approx b\left(\frac{v}{b^3}\right)^{(1+3x)/5} N^{(3+4x)/5} \phi^x$$

Chains in semidilute solutions are random walks $\frac{3+4x}{5} = \frac{1}{2} \rightarrow \mathbf{x = -1/8}$

$$R \approx R_F \left(\frac{\phi}{\phi^*}\right)^{-1/8} \approx b\left(\frac{v}{b^3 \phi}\right)^{1/8} N^{1/2}$$

Similarly correlation length $\xi \approx R_F \left(\frac{\phi}{\phi^*}\right)^y \approx b\left(\frac{v}{b^3}\right)^{(1+3y)/5} N^{(3+4y)/5} \phi^y$

is independent of N in

semidilute solution $3 + 4y = 0$ $\mathbf{y = -3/4}$ $\xi \approx R_F \left(\frac{\phi}{\phi^*}\right)^{-3/4} \approx b\left(\frac{b^3}{v}\right)^{1/4} \phi^{-3/4}$

Concentrated Solutions

Correlation length ξ decreases with concentration, while thermal blob size ξ_T is independent of concentration.

At concentration ϕ^{**} the two lengths are equal $\xi \approx \xi_T$ and intermediate swollen regime disappears.

$$\phi^{**} \approx \frac{\nu}{b^3} \quad \xi \approx b \left(\frac{b^3}{\nu} \right)^{1/4} \phi^{-3/4} \approx \frac{b^4}{\nu} \approx \xi_T$$

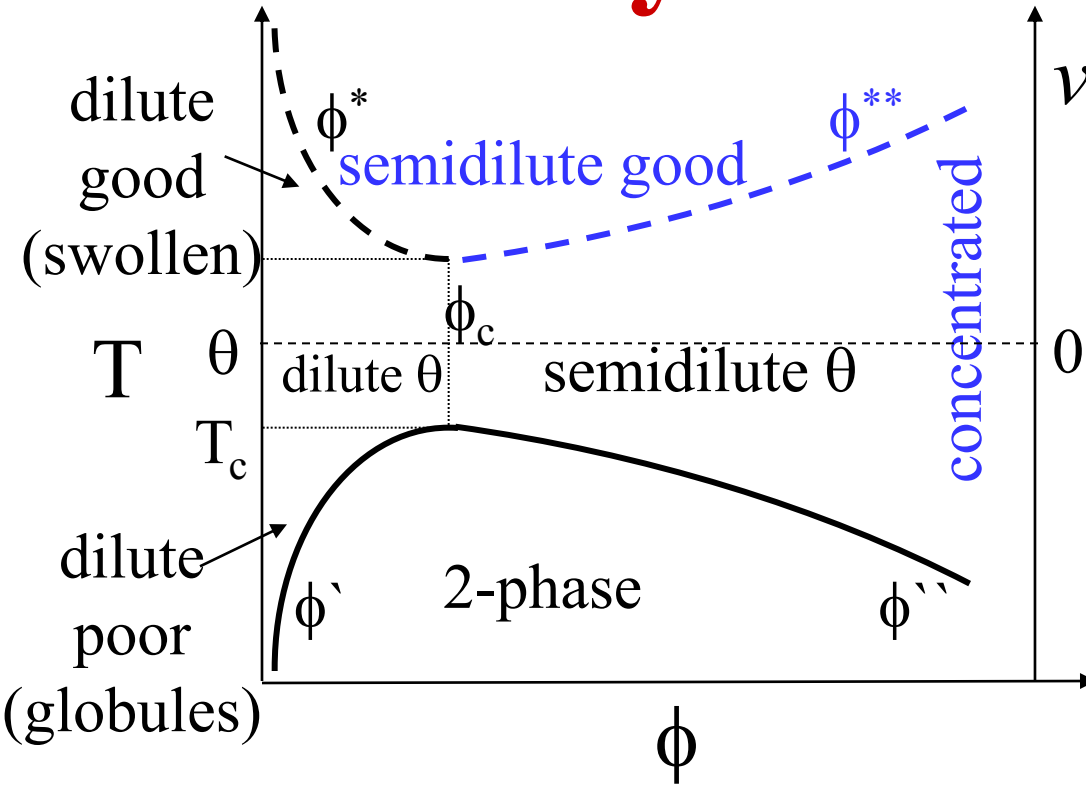
This concentration is analogous to ϕ'' in poor solvent at which two- and three-body interactions are balanced.

In concentrated solutions chains are ideal at all length scales.

On length scales less than ξ chains are ideal because excluded volume interactions are weaker than kT .

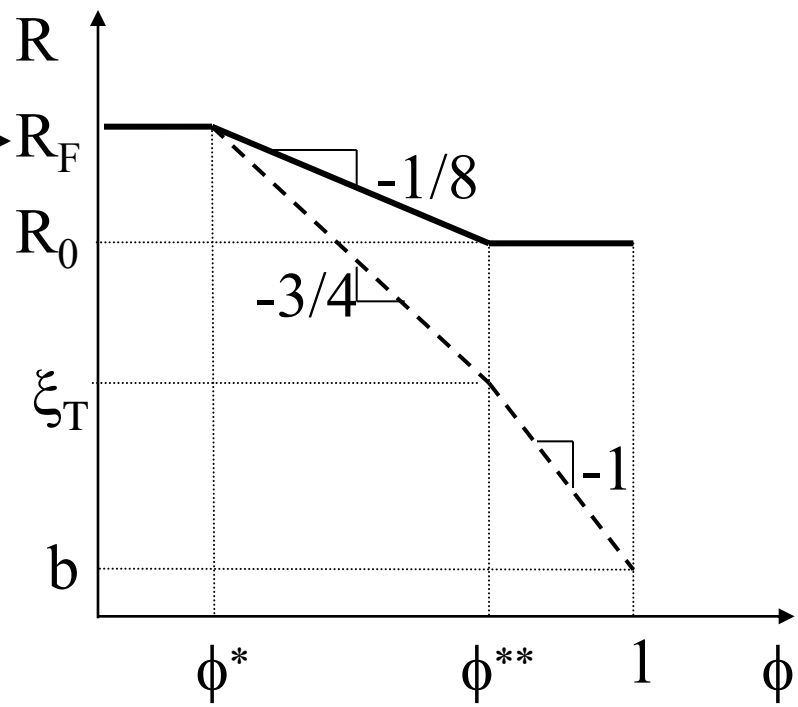
On length scales larger than ξ chains are ideal because excluded volume interactions are screened by surrounding chains.

Polymer Solutions



$$R \approx R_0 \left(\frac{\phi}{\phi^{**}} \right)^{-1/8}$$

for $\phi^* < \phi < \phi^{**}$



In athermal solvent $v \approx b^3$ $\xi_T \approx b$

$$\xi \approx \frac{b}{\phi^{3/4}}$$

$$R \approx \frac{bN^{1/2}}{\phi^{1/8}}$$

$$\phi^{**} \approx 1$$

Osmotic Pressure

In dilute solutions $\phi < \phi^*$ - van't Hoff Law $\Pi \approx \frac{kT}{b^3} \frac{\phi}{N}$

Osmotic pressure Π in semidilute solutions $\phi > \phi^*$ is a stronger function of concentration

$$\Pi \approx \frac{kT}{b^3} \frac{\phi}{N} f\left(\frac{\phi}{\phi^*}\right) \quad f\left(\frac{\phi}{\phi^*}\right) \approx \begin{cases} 1 & \text{for } \phi < \phi^* \\ (\phi/\phi^*)^z & \text{for } \phi > \phi^* \end{cases}$$

Osmotic pressure in semidilute solutions

$$\Pi \approx \frac{kT}{b^3} \frac{\phi}{N} \left(\frac{\phi}{\phi^*}\right)^z \approx \frac{kT}{b^3} \phi^{1+z} \left(\frac{v}{b^3}\right)^{3z/5} N^{4z/5-1}$$

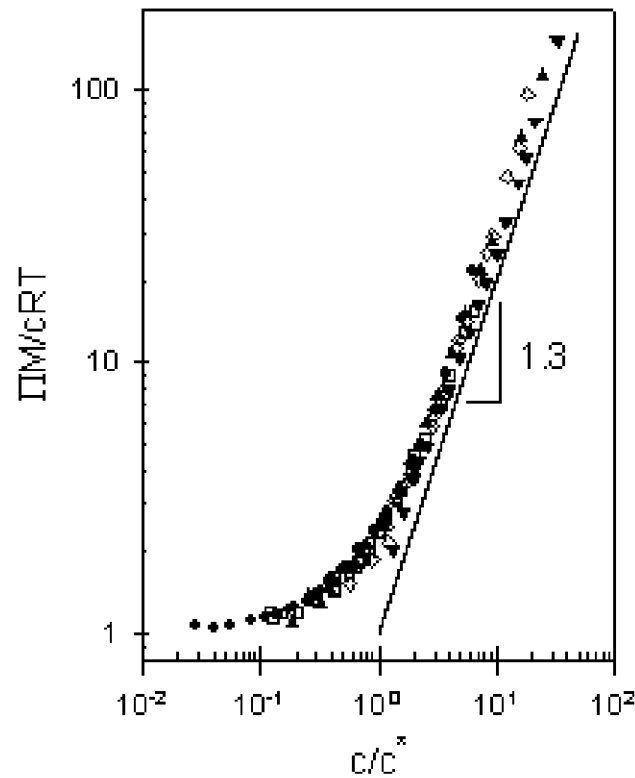
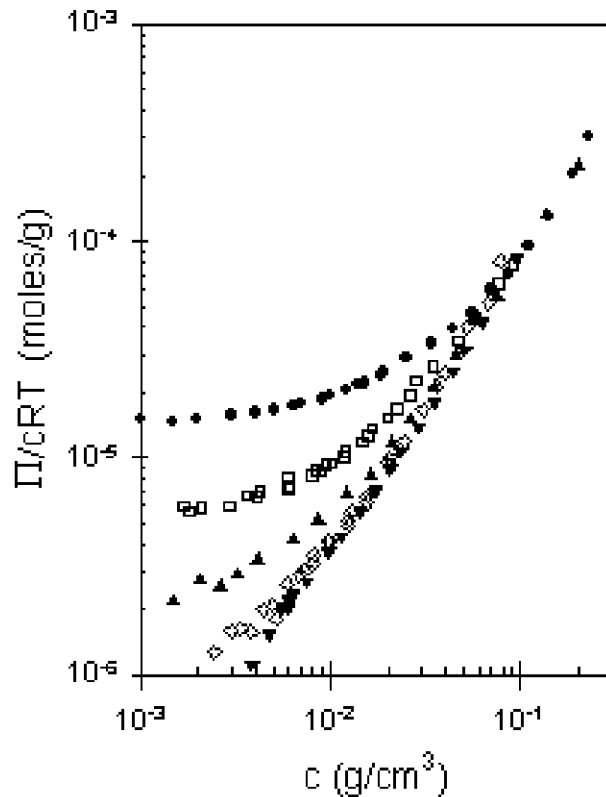
is independent of chain length ($4z/5-1=0$). $z=5/4$

$$\Pi \approx \frac{kT}{b^3} \left(\frac{v}{b^3}\right)^{3/4} \phi^{9/4} \approx \frac{kT}{\xi^3}$$

Neighboring blobs repel each other with energy of order kT .

Concentration Dependence of Osmotic Pressure

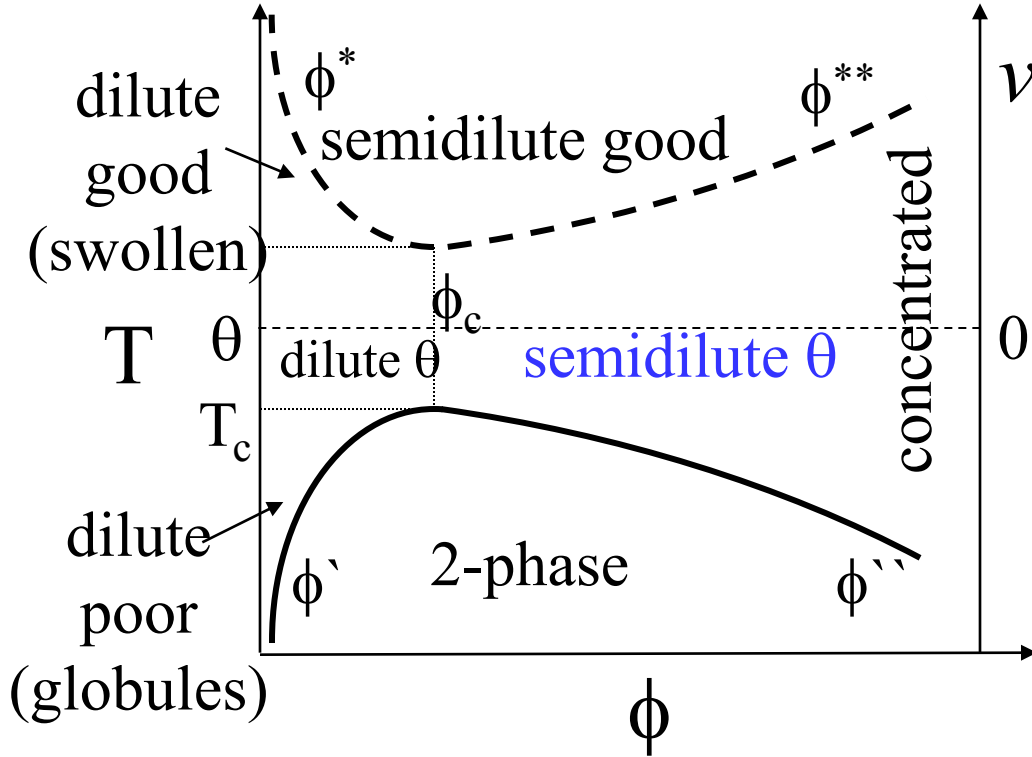
$$\frac{\Pi b^3 N}{kT\phi} \approx f\left(\frac{\phi}{\phi^*}\right) \approx 1 + \left(\frac{\phi}{\phi^*}\right)^{1.3}$$



Poly(α -methylstyrene) in toluene at 25 °C

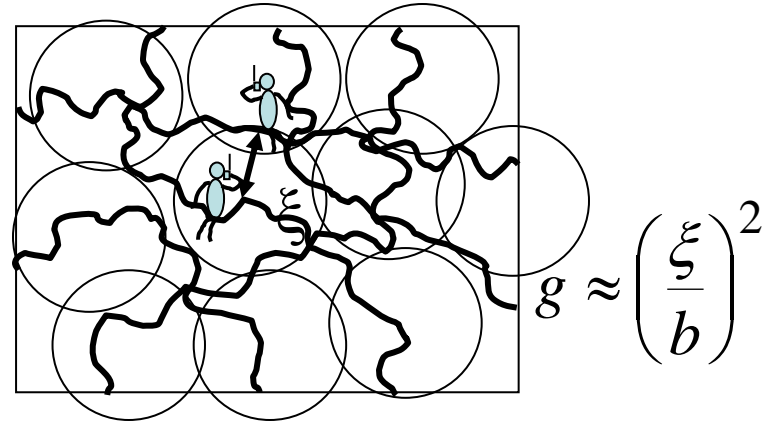
Noda et al, Macromol. **16**, 668, 1981

Semidilute Theta Solutions



Chains are almost ideal

$$R \approx bN^{1/2}$$



Correlation blobs are space-filling $\phi \approx \frac{b^3 g}{\xi^3} \approx \frac{b^3 (\xi/b)^2}{\xi^3} \approx \frac{b}{\xi} \quad \xi \approx \frac{b}{\phi}$

$\xi \approx R_0 \approx b\sqrt{N}$ at $\phi^* \approx \frac{Nb^3}{R_0^3} \approx \frac{1}{\sqrt{N}}$

Scaling assumption for $\phi > \phi^*$ $\xi \approx bN^{1/2} \left(\frac{\phi}{\phi^*}\right)^x \approx b\phi^x N^{(1+x)/2}$

Correlation length in semidilute solutions

is independent of chain length $(1+x)/2 = 0$

$x = -1$

$\xi \approx \frac{b}{\phi}$

Quiz # 2

What is the meaning of correlation length in semidilute theta solutions?

How different are semidilute theta solutions from ideal solutions of ideal chains?

Osmotic Pressure in Semidilute Theta Solutions

Mean-field prediction $\Pi = \frac{kT}{b^3} \left(\frac{\phi}{N} + \frac{w}{b^6} \phi^3 + \dots \right)$

First term (van't Hoff law) is important in dilute solutions

Three-body term is larger than linear

in semidilute solutions $\phi > 1/N^{1/2}$

$$\Pi = \frac{kT}{b^3} \phi^3$$

Scaling Theory

$$\Pi \approx \frac{kT}{b^3} \frac{\phi}{N} h\left(\frac{\phi}{\phi^*}\right) \quad h\left(\frac{\phi}{\phi^*}\right) \approx \begin{cases} 1 & \text{for } \phi < \phi^* \\ (\phi/\phi^*)^y & \text{for } \phi > \phi^* \end{cases}$$

Osmotic pressure in semidilute θ -solutions

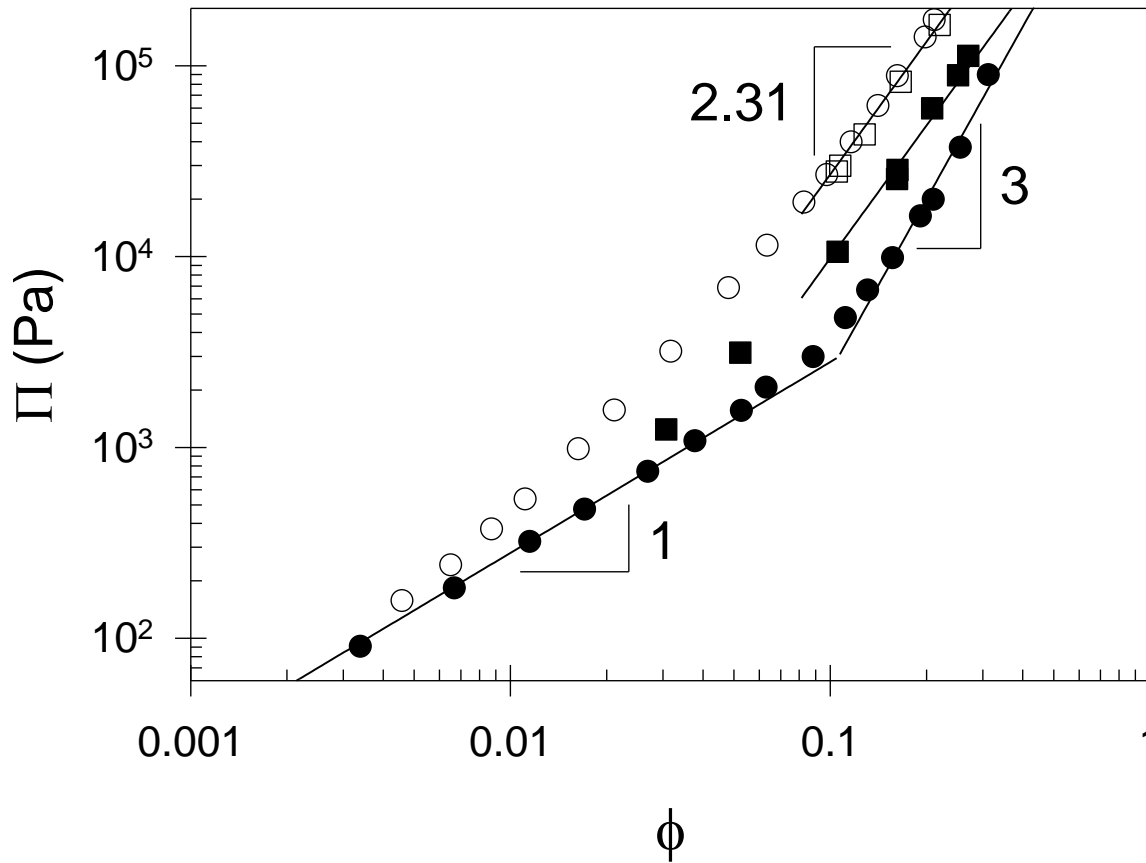
$$\Pi \approx \frac{kT}{b^3} \frac{\phi}{N} \left(\frac{\phi}{\phi^*}\right)^y \approx \frac{kT}{b^3} \phi^{1+y} N^{y/2-1}$$

is independent of chain length ($y/2-1=0$).

$y=2$

$$\Pi \approx \frac{kT}{b^3} \phi^3 \approx \frac{kT}{\xi^3}$$

Osmotic Pressure



Polyisobutylene in benzene at $\theta=24.5$ °C (filled circles), in benzene at 50 °C (filled squares), in cyclohexane at 30 °C (open circles) and at 8 °C (open squares)
 Flory and Daoust J. Polym. Sci. **25**, 429, 1957

$$\xi \approx \frac{b}{\phi}$$

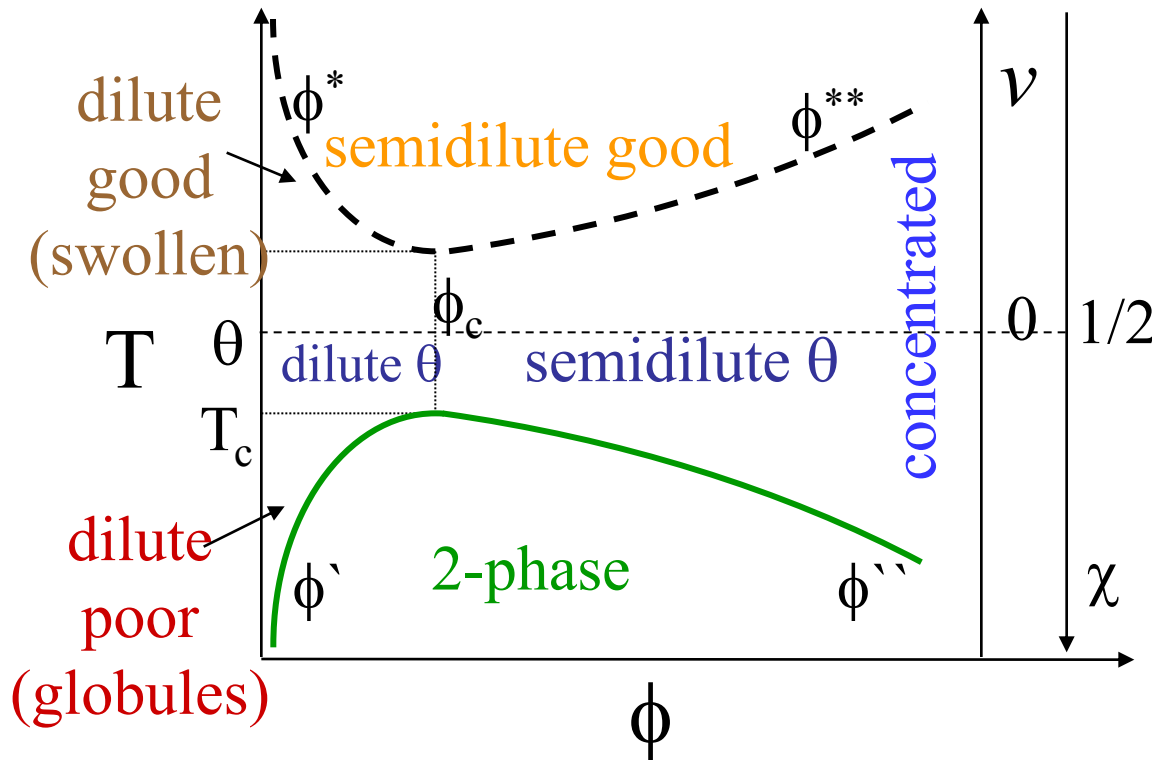
$$\Pi \approx \frac{kT}{\xi^3} \approx \frac{kT}{b^3} \phi^3$$

Correlation length in semidilute θ -solvents is of the order of the distance between 3-body contacts.

Number density of n-body contacts $\sim \phi^n/b^3$

Distance between n-body contacts in 3-dimensional space $r_n \approx b\phi^{-n/3}$

Summary of Polymer Solutions



In poor solvent part of the diagram **binodal** separates **2-phase** from 2 single phase regions:

Dilute globules at low concentrations $\phi < \phi'$

Concentrated solutions with overlapping ideal chains at $\phi > \phi''$

Near θ -temperature there are **dilute** and **semidilute θ -regimes** with ideal chains.

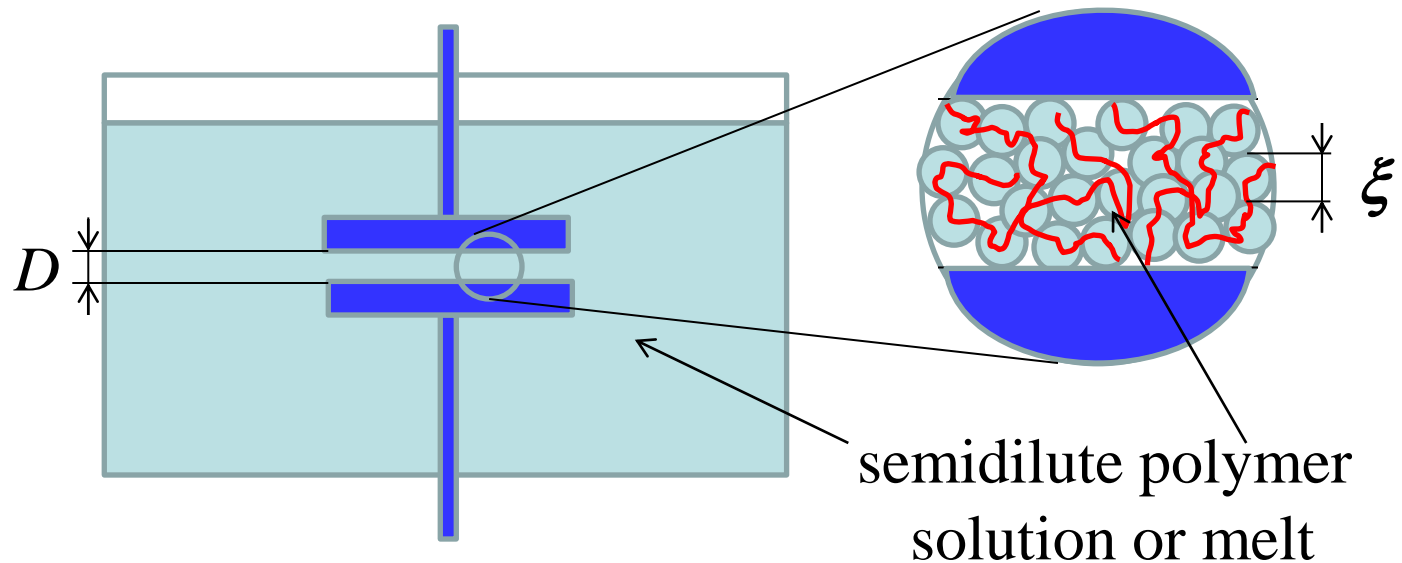
Dilute good solvent regime with swollen chains at $\phi < \phi^*$ and $\nu > 0$.

Semidilute good solvent regime at $\phi^* < \phi < \phi^{**}$ with chains swollen at intermediate length scales shorter than correlation length ξ .

Osmotic pressure in semidilute solutions is kT per correlation volume ξ^3 .

Challenge Problem 5:

Confinement of Polymers in Solutions & Melt



Calculate the pressure between two solid plates fully immersed into a semidilute polymer solution or melt as a function of separation D between plates for separations smaller than chain size R .

Assume no attraction between plates and polymer.

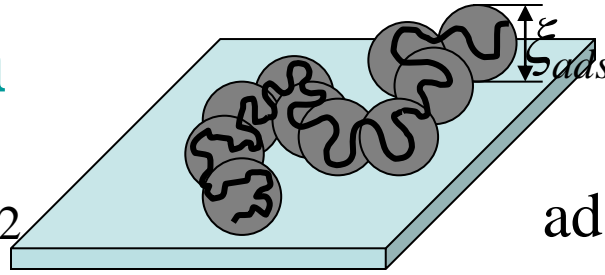
Separately consider cases with correlation length $\xi < D < R$ and $b < D < \xi$

Single Chain Adsorption

Ideal chain

adsorption blob

$$\xi_{ads} \approx bg^{1/2}$$



Real chain

adsorption blob $\xi_{ads} \approx bg^{3/5}$

Volume fraction in a chain section of size ξ_{ads} containing g monomers

$$\phi \approx \frac{b^3 g}{\xi_{ads}^3} \approx \frac{b}{\xi_{ads}}$$

$$\phi \approx \frac{b^3 g}{\xi_{ads}^3} \approx \left(\frac{b}{\xi_{ads}} \right)^{4/3}$$

Number of monomers per adsorption blob in contact with the surface

$$\frac{\phi}{b^3} \xi_{ads}^2 b \approx \frac{\xi}{b}$$

$$\frac{\phi}{b^3} \xi_{ads}^2 b \approx \left(\frac{\xi}{b} \right)^{2/3}$$

Energy gain per monomer in contact with the surface is $-\epsilon kT$

Energy gain per adsorption blob

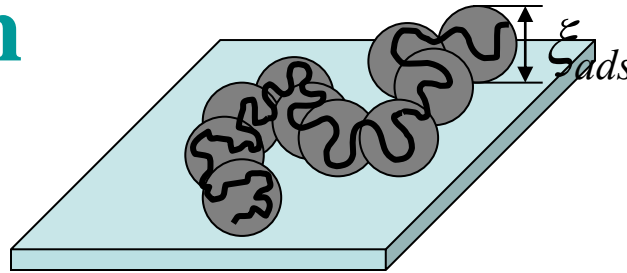
$$kT\epsilon \frac{\xi_{ads}}{b} \approx kT$$

$$kT\epsilon \left(\frac{\xi_{ads}}{b} \right)^{2/3} \approx kT$$

Single Chain Adsorption

Ideal chain

$$\varepsilon \frac{\xi_{ads}}{b} \approx 1$$



Real chain

$$\varepsilon \left(\frac{\xi_{ads}}{b} \right)^{2/3} \approx 1$$

Size ξ_{ads} and number of monomers g in an adsorption blob

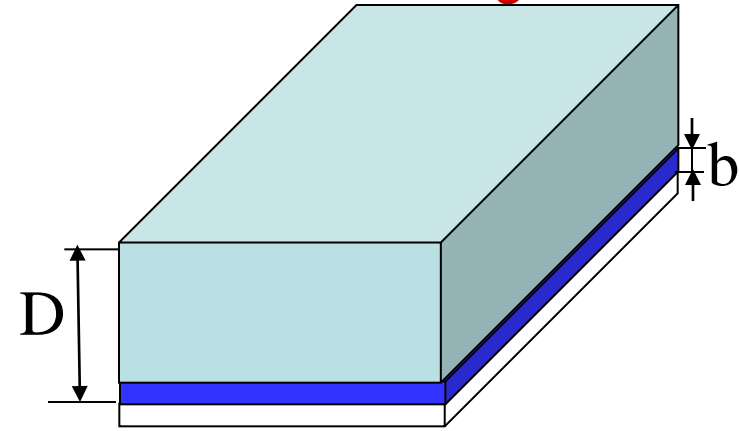
$$\xi_{ads} \approx \frac{b}{\varepsilon} \quad g \approx \left(\frac{\xi_{ads}}{b} \right)^2 \approx \varepsilon^{-2} \quad \xi_{ads} \approx \frac{b}{\varepsilon^{3/2}} \quad g \approx \left(\frac{\xi_{ads}}{b} \right)^{5/3} \approx \varepsilon^{-5/2}$$

Free energy of an adsorbed chain

$$F \approx -kT \frac{N}{g} \approx -kTN\varepsilon^2$$

$$F \approx -kT \frac{N}{g} \approx -kTN\varepsilon^{5/2}$$

Flory Theory of Adsorption



Fraction of monomers in direct contact with the surface is b/D

Number of monomers in direct contact with the surface is Nb/D

Energy gain per monomer contact with the surface is $-kT\varepsilon$

Energy gain from surface interactions per chain $F_{\text{int}} \approx -\varepsilon kTN \frac{b}{D}$

Total free energy is a sum of interaction and confinement parts

Ideal chain

$$F = F_{\text{conf}} + F_{\text{int}}$$

Real chain

$$F \approx kTN \left(\frac{b}{D} \right)^2 - kT\varepsilon N \frac{b}{D}$$

$$F \approx kTN \left(\frac{b}{D} \right)^{5/3} - kT\varepsilon N \frac{b}{D}$$

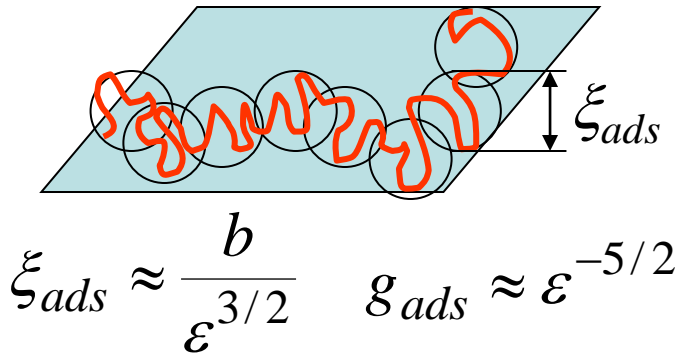
Optimal thickness

$$D \approx \frac{b}{\varepsilon}$$

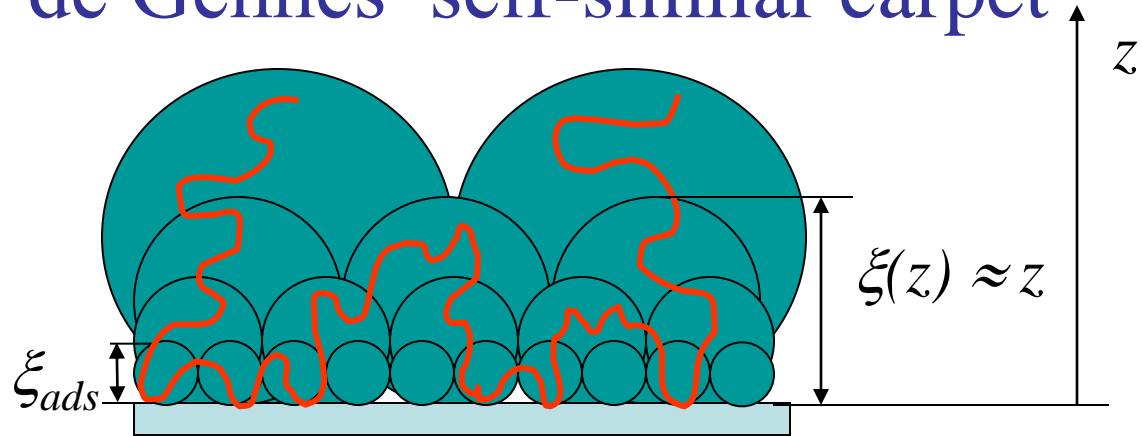
$$D \approx \frac{b}{\varepsilon^{3/2}}$$

Multi-Chain Adsorption

Single-chain adsorption



de Gennes' self-similar carpet



First layer is dense packing of adsorption blobs

Polymer concentration decays from the high value in the first layer.

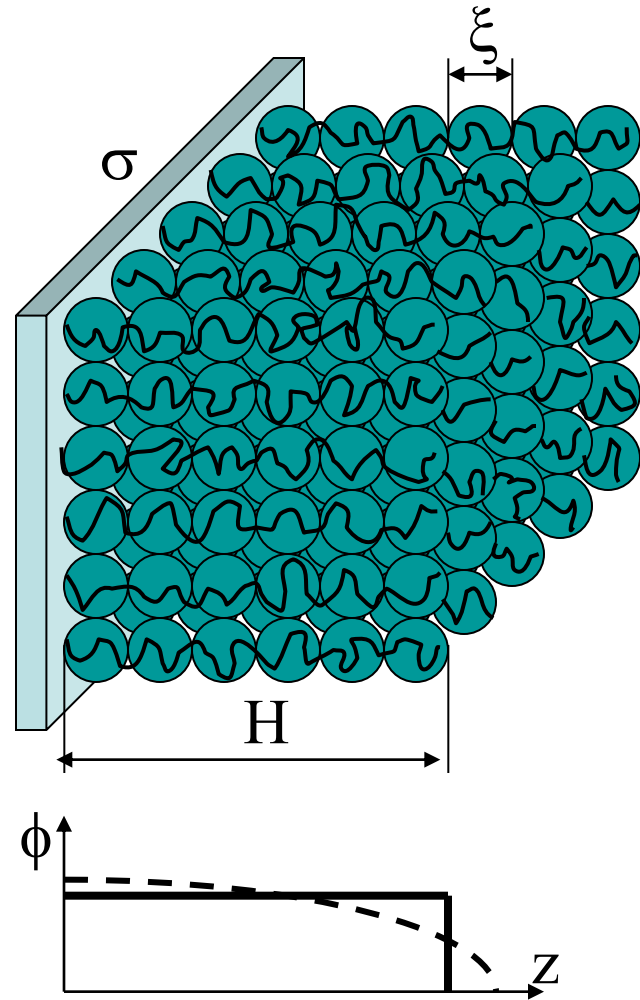
The correlation length $\xi(z)$ corresponding to concentration $\phi(z)$ at distance z from the surface is of the order of this distance.

$$\xi(z) \approx \frac{b}{[\phi(z)]^{3/4}} \approx z \quad \phi(z) \approx \left(\frac{z}{b}\right)^{-4/3}$$

Coverage is controlled by the first layer of blobs.

$$\Gamma \approx \int \frac{\phi(z)}{b^3} dz \approx b^{-3} \int_{\xi_{ads}}^R \left(\frac{z}{b}\right)^{-4/3} dz \approx b^{-2} \left(\frac{b}{\xi_{ads}}\right)^{1/3} \approx \frac{\varepsilon^{1/2}}{b^2} \approx \frac{g_{ads}}{\xi_{ads}^2}$$

Alexander – de Gennes Brush



Grafting density σ – number of chains per unit area.

Distance between sections of chains

$$\xi = \sigma^{-1/2}$$

Number of monomers per blob

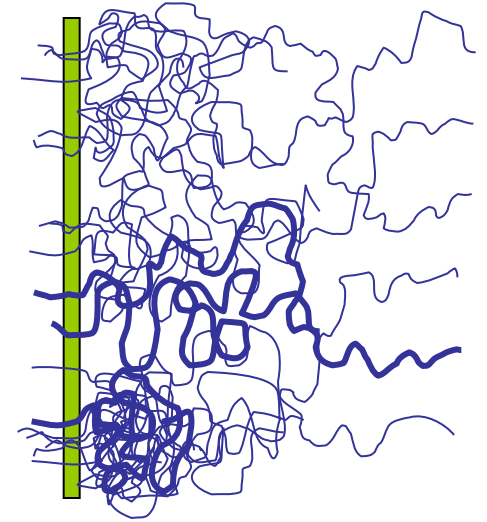
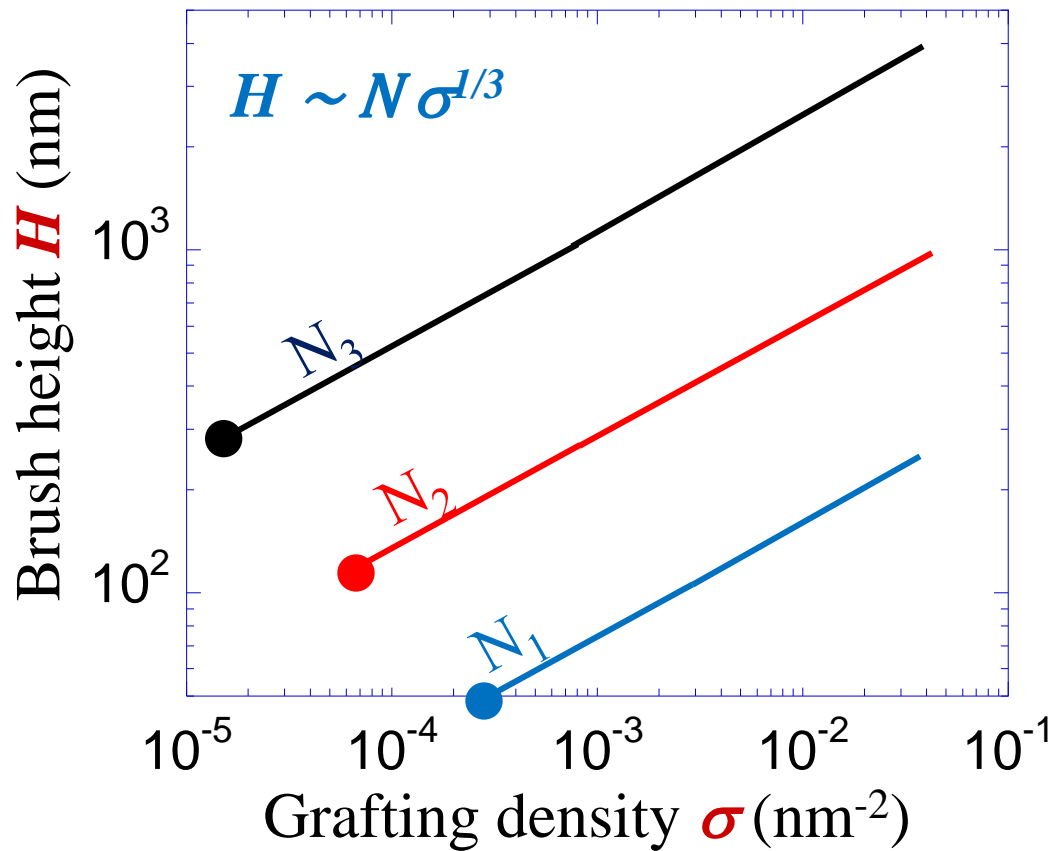
$$g \sim \xi^{1/\nu} \sim \sigma^{1/(2\nu)}$$

Thickness of the brush $H \sim \xi N/g \sim N\sigma^{(1-\nu)/(2\nu)}$

Energy per chain $E_{chain} \sim kT N/g \sim kTN\sigma^{1/(2\nu)}$

Energy per unit volume $\frac{E_{chain}}{V} \approx E_{chain} \frac{\sigma}{H} \approx kT \frac{N}{g} \frac{\sigma}{H} \approx kT \frac{\sigma}{\xi} \approx \frac{kT}{\xi^3} \approx \Pi$

Polymer Brush Height depends on Grafting Density



Mushroom Regime
unperturbed size
 $H \simeq R_0$

If the grafting density is high, chains repel each other and stretch away from the surface, forming a polymer brush.

