Introduction to Polymer Theory

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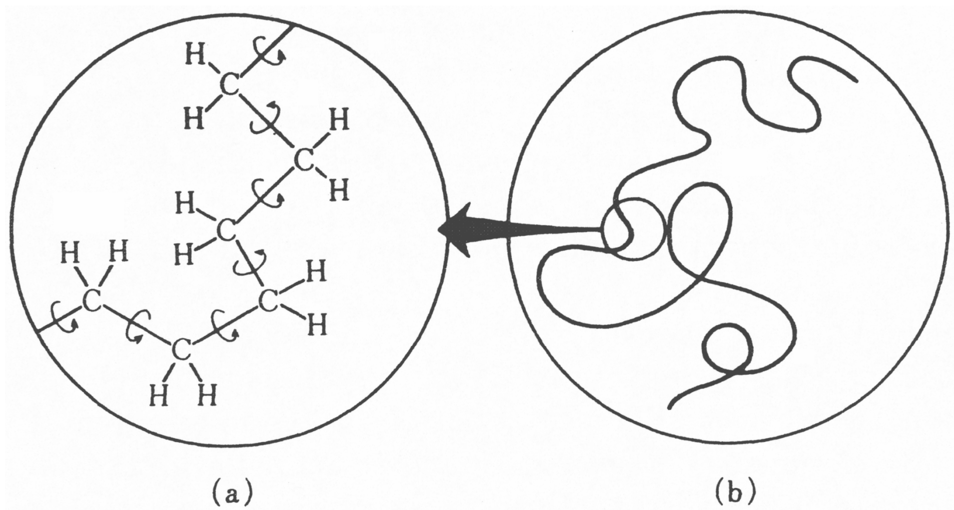
Introduction

chemical details vs. universal properties

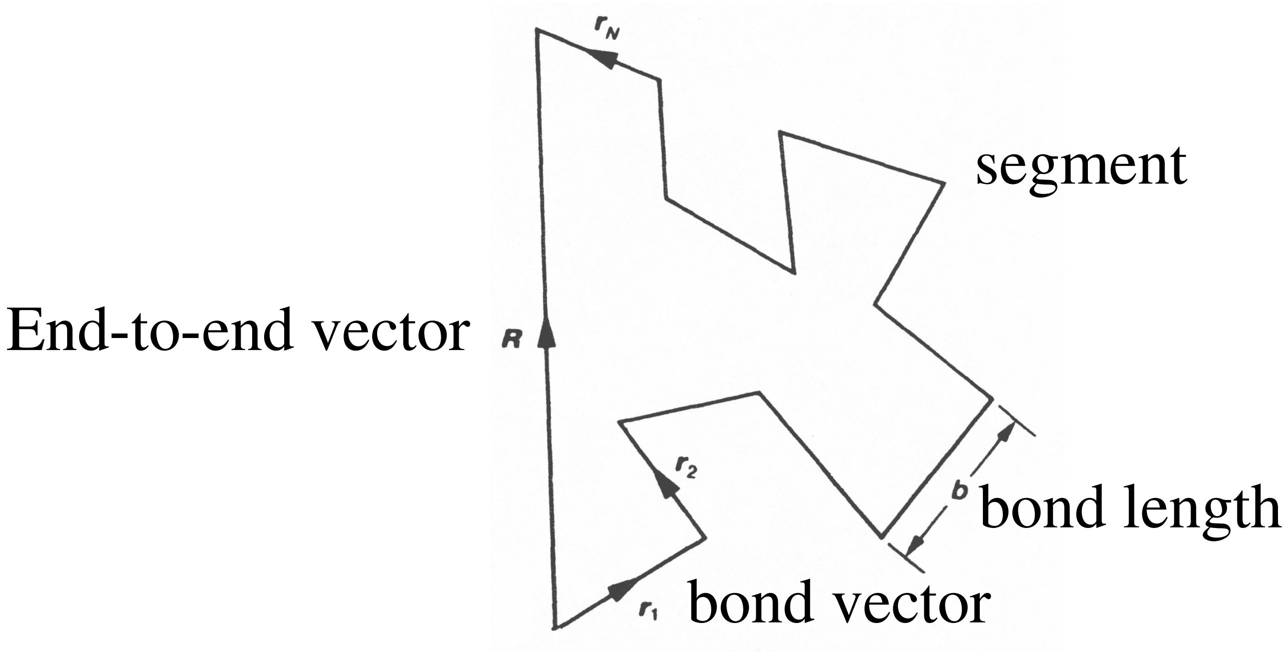


A polymer is a **statistical mechanical** system,
for which the role of **entropy** is very important

Programme

1. Ideal polymers:
   - conformations: Gaussian coil
   - in an external field
   - in a Self Consistent Field (SCF)
2. Non-ideal polymers
   - excluded volume
   - attractions
3. Concentrated solutions:
   - Flory-Huggins theory
   - scaling theory (semi-dilute solutions)

Polymer conformations



End-to-end vector: $\vec{R} = \sum_{i=1}^{N} \vec{r}_i$

$\langle \vec{R} \rangle = 0$

Polymer conformations

End-to-end vector: $\vec{R} = \sum_{i=1}^{N} \vec{r}_i$

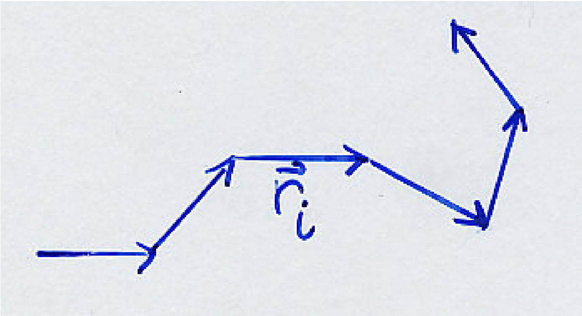
$$\langle \vec{R}^2 \rangle = \langle \vec{R} \bullet \vec{R} \rangle = \left\langle \sum_{i=1}^{N} \sum_{j=1}^{N} \vec{r}_i \bullet \vec{r}_j \right\rangle$$

$$= \sum_{i=1}^{N} \langle \vec{r}_i^{\,2} \rangle + \sum_{i=1}^{N} \sum_{j \neq i} \langle \vec{r}_i \bullet \vec{r}_j \rangle$$

$\propto N$ $\propto N$ smaller if $|j-i|$ larger

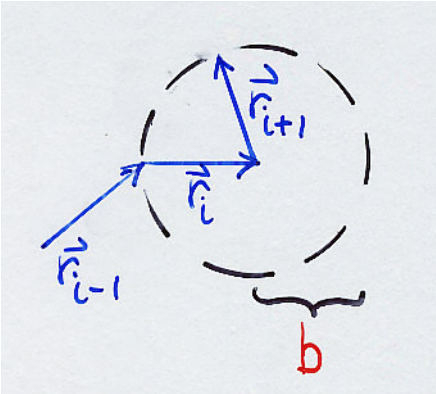
$$\langle \vec{R}^2 \rangle \propto N$$

$$\sqrt{\langle \vec{R}^2 \rangle} \propto N^{1/2}$$



Chain models (1)

Freely jointed chain:



$$\left\langle \vec{r}_i^{\,2} \right\rangle = \left\langle \vec{r}_i \bullet \vec{r}_i \right\rangle = b^2$$

$$\left\langle \vec{r}_i \bullet \vec{r}_j \right\rangle = 0 \quad (i \neq j)$$

$$\left\langle \vec{R}^2 \right\rangle = \sum_{i=1}^{N} \left\langle \vec{r}_i^{\,2} \right\rangle + \sum_{i=1}^{N} \sum_{j \neq i} \left\langle \vec{r}_i \bullet \vec{r}_j \right\rangle = Nb^2 \; (+\,0)$$

Chain models (2)

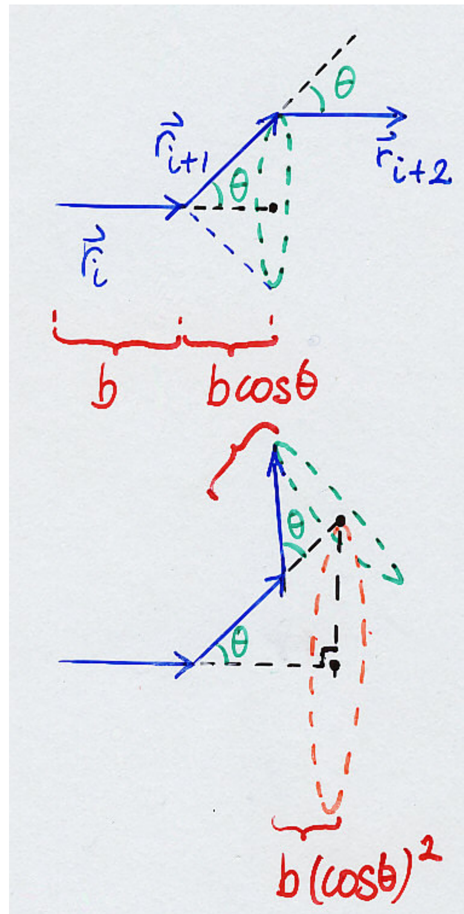
Freely rotating chain:

$$\left\langle \vec{r}_i^{\,2} \right\rangle = \left\langle \vec{r}_i \bullet \vec{r}_i \right\rangle = b^2$$

$$\left\langle \vec{r}_i \bullet \vec{r}_{i+1} \right\rangle = b^2 \left(\cos\theta\right)^1$$

$$\left\langle \vec{r}_i \bullet \vec{r}_{i+2} \right\rangle = b^2 \left(\cos\theta\right)^2$$

$$\boxed{\left\langle \vec{r}_i \bullet \vec{r}_j \right\rangle = b^2 \left(\cos\theta\right)^{|j-i|}}$$



Chain models (3)

$$\left\langle \vec{R}^2 \right\rangle = \sum_{i=1}^{N} b^2 \left[1 + (\cos\theta)^1 + (\cos\theta)^2 + (\cos\theta)^3 + \cdots \right] = Nb^2 \, \frac{1+\cos\theta}{1-\cos\theta}$$

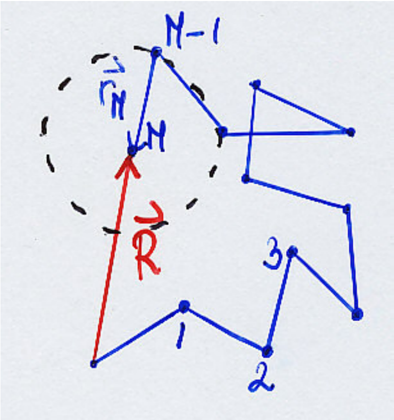
$$= Nb_{eff}^{\;2} \qquad \text{with} \quad b_{eff} \equiv b\sqrt{\frac{1+\cos\theta}{1-\cos\theta}}$$

General result when NO INTERACTION between segments

$$\left\langle \vec{R}^2 \right\rangle = Nb_{eff}^{\;2} \qquad \text{with more general} \quad b_{eff}$$

End-to-end distribution (1)

$P(\vec{R}, N)$: probability of finding $\vec{R}$ after N segments?



recursion relation:

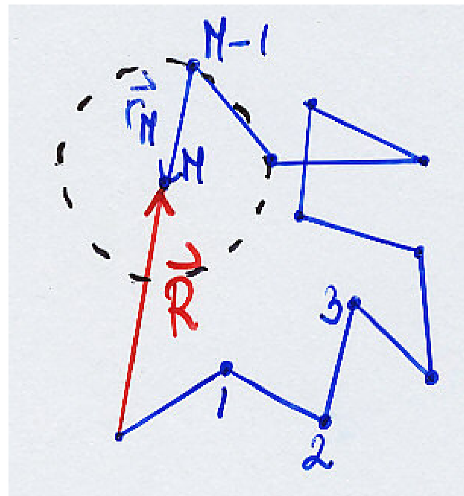
$$P(\vec{R}, N) = \left\langle P(\vec{R} - \vec{r}_N, N-1) \right\rangle_{\vec{r}_N}$$

Taylor expansion $(N \gg 1$ and $\vec{R} \gg \vec{r}_N)$:

$$P(\vec{R} - \vec{r}_N, N-1) \approx P(\vec{R}, N) + \frac{\partial P}{\partial N}(-1) + \sum_{\alpha=x,y,z} \frac{\partial P}{\partial \alpha}\left(-\vec{r}_{N,\alpha}\right)$$

$$+ \frac{1}{2} \sum_{\alpha=x,y,z} \sum_{\alpha=x,y,z} \frac{\partial^2 P}{\partial \alpha \partial \beta}\left(-\vec{r}_{N,\alpha}\right)\left(-\vec{r}_{N,\beta}\right) + \cdots$$

End-to-end distribution (2)



apply $\left\langle \cdots \right\rangle_{\vec{r}_N}$: $\left\langle \vec{r}_N \right\rangle_{\vec{r}_N} = 0$

$$\left\langle \vec{r}_{N\alpha} \vec{r}_{N\beta} \right\rangle_{\vec{r}_N} = \left\langle \vec{r}_{N\alpha} \right\rangle_{\vec{r}_N} \left\langle \vec{r}_{N\beta} \right\rangle_{\vec{r}_N} = 0 \qquad (\alpha \neq \beta)$$

$$\left\langle \vec{r}_{Nx}{}^2 \right\rangle_{\vec{r}_N} = \left\langle \vec{r}_{Ny}{}^2 \right\rangle_{\vec{r}_N} = \left\langle \vec{r}_{Nz}{}^2 \right\rangle_{\vec{r}_N} = \frac{1}{3} b^2$$

End-to-end distribution (3)

$$P(\vec{R},N) \approx P(\vec{R},N) + \frac{\partial P}{\partial N}(-1) + \frac{1}{6}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)P + \cdots$$

With the definition of the Laplacian $\Delta \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

we thus find that $P(\vec{R},N)$ is the solution of:

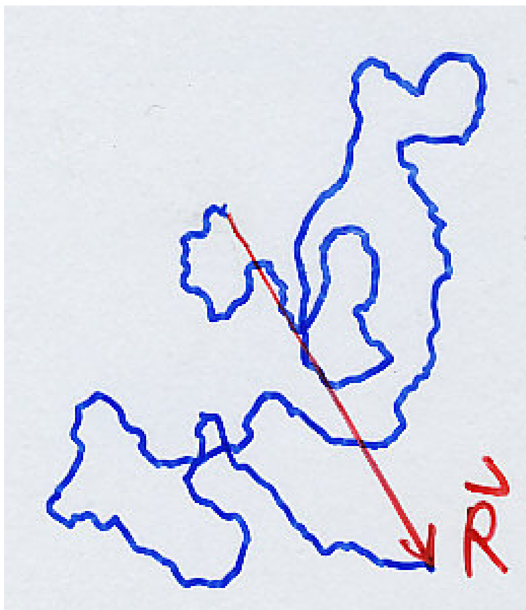
$$\frac{\partial P(\vec{R},N)}{\partial N} = \frac{b^2}{6}\Delta P(\vec{R},N)$$

cf. the diffusion equation for $c(\vec{R},t)$:

$$\frac{\partial c(\vec{R},t)}{\partial t} = D\Delta c(\vec{R},t)$$

End-to-end distribution (4)

Cf. one diffusing colloidal particle (Einstein):



$$\left\langle \vec{R}^2 \right\rangle = 6Dt$$

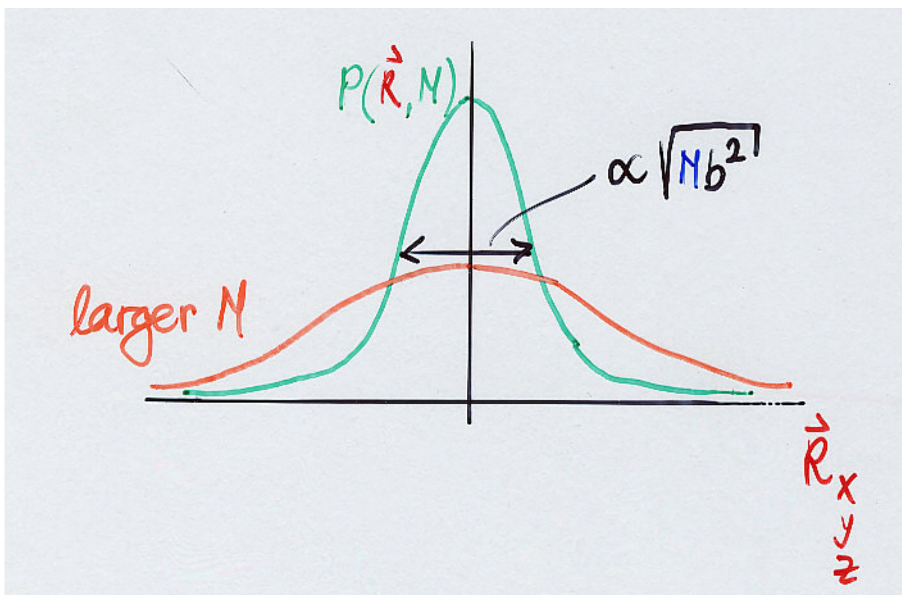
$$b^2 \quad N$$

An (ideal) polymer is like the **trajectory** of a diffusing particle!

End-to-end distribution (5)

The solution of $\frac{\partial P(\vec{R},N)}{\partial N} = \frac{b^2}{6}\Delta P(\vec{R},N)$ is (by analogy):

$$P(\vec{R},N) = \left(\frac{3}{2\pi N b^2}\right)^{3/2} \exp\left(-\frac{3\vec{R}^2}{2Nb^2}\right)$$



Central Limit Theorem

Consider the sum of N independent, stochastic variables (N is large).

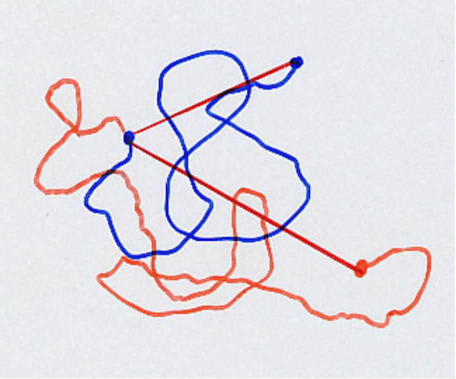
This sum has a normal (= Gaussian) distribution with $\sigma^2 \propto N$.

$$\vec{R} = \sum_{i=1}^{N} \vec{r}_i \quad \Rightarrow \quad \sigma_{\vec{R}}{}^2 = \left\langle \left(\vec{R} - 0\right)^2 \right\rangle = \left\langle \vec{R}^2 \right\rangle \propto N \left(\times b_{eff}{}^2\right)$$

Variation in $\vec{R}^2$:

$$\sigma_{\vec{R}^2} = \sqrt{\left\langle \left(\vec{R}^2 - \left\langle \vec{R}^2 \right\rangle\right)^2 \right\rangle} = \sqrt{\frac{2}{3}} N b^2$$

A Gaussian coil is a *strongly fluctuating object*!



Conclusion: many (global) properties of polymers do not depend on the (local) details of the model.

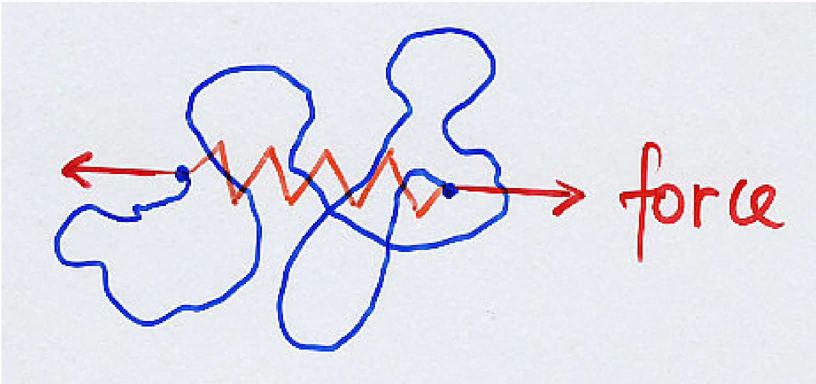
Entropy of a Gaussian coil

$$S(\vec{R}) = k_B \ln W$$

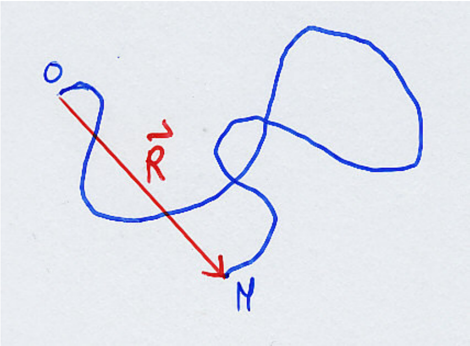
$$= \text{cst} + k_B \ln P(\vec{R})$$

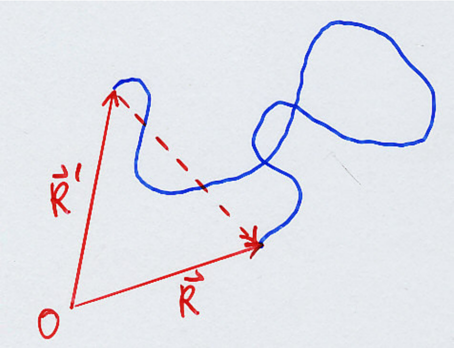
$$= \text{cst} - \frac{3k_B}{2Nb^2}\vec{R}^2$$

$$A(\vec{R})\left(= -TS\right) = \text{cst} + \frac{3k_B T}{2Nb^2}\vec{R}^2$$ ENTROPIC SPRING



Conditional probability



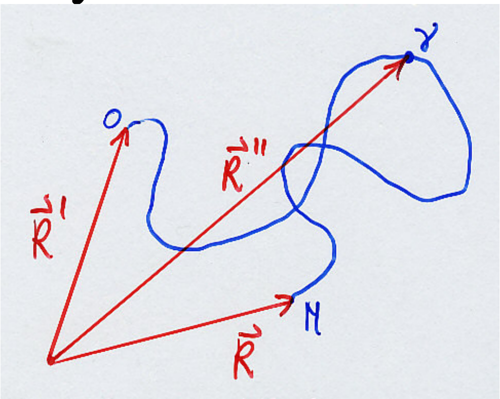


probability

$P(\vec{R}, N) = G_N(\vec{R} \mid 0)$

conditional probability

$G_N(\vec{R} \mid \vec{R}')$



independent end points: $G_\nu(\vec{R}'' \mid \vec{R}')\, G_{N-\nu}(\vec{R} \mid \vec{R}'')$

integrate over R'' $\Rightarrow$ $G_N(\vec{R} \mid \vec{R}')$

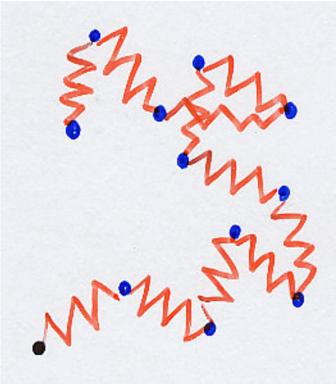
(OK for Gaussian chains)

Additional polymer models

Gaussian bond model:

Every single bond Gaussian $\propto \exp\left(-\frac{3\,\vec{r}_i^{\,2}}{2(1)b^2} \right)$

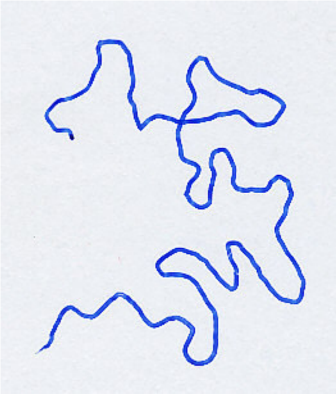
Bead-spring model:



spring constant: $\frac{3k_BT}{2(1)b^2}$

(used in the Rouse/Zimm models for polymer dynamics)

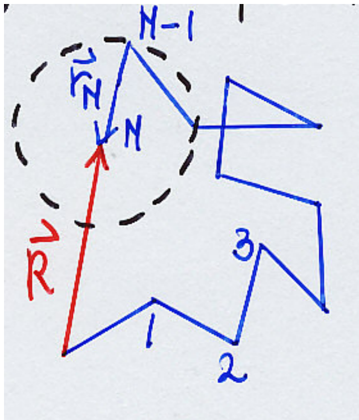
Continuous model:



permits the use of path integrals

A polymer in an external field (1)

assume a segment at position $\vec{R}$ has energy $\varphi(\vec{R})$



the recursion relation now changes to:

$$P(\vec{R},N) = \left\langle P(\vec{R}-\vec{r}_N, N-1)\right\rangle_{\vec{r}_N} \exp\left(-\frac{\varphi(\vec{R})}{k_B T}\right)$$

Taylor expansion:

$$P(\vec{R}-\vec{r}_N, N-1) \approx \left(P(\vec{R},N) + \frac{\partial P}{\partial N}(-1) + \cdots \text{etc.} \right) \times \left(1 - \frac{\varphi(\vec{R})}{k_B T} + \cdots \right)$$

$$\boxed{\frac{\partial P}{\partial N} = \frac{b^2}{6}\Delta P - \frac{\varphi(\vec{R})}{k_B T} P}$$

cf. diffusion in an external field

A polymer in an external field (2)

similarly for the conditional probability $G_N(\vec{R} \mid \vec{R}')$

$$-\frac{\partial G}{\partial N} = -\frac{b^2}{6}\Delta G + \frac{\varphi(\vec{R})}{k_B T} G$$

$\vec{R}'$ is a parameter, but: $\vec{R} \leftrightarrow \vec{R}'$

cf. $-i\hbar\frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\Delta\psi + V(\vec{R})\psi$

QM: time-dependent Schroedinger equation for $\psi\left(\vec{R},t\right)$

linear, partial differential equations; **solution method:**

separation of variables

Separation of variables

$$-\frac{\partial G}{\partial N} = -\frac{b^2}{6}\Delta G + \frac{\varphi(\vec{R})}{k_B T} G$$

assume G can be written as: $G = f(N)\psi(\vec{R})$

$$-\psi(\vec{R})\frac{\partial f(N)}{\partial N} = -\frac{b^2}{6} f(N)\Delta\psi(\vec{R}) + \frac{\varphi(\vec{R})}{k_B T} f(N)\psi(\vec{R})$$

divide by $f(N)\psi(\vec{R})$:

$$-\frac{1}{f(N)}\frac{\partial f(N)}{\partial N} = -\frac{b^2}{6}\frac{\Delta\psi(\vec{R})}{\psi(\vec{R})} + \frac{\varphi(\vec{R})}{k_B T} \quad = \lambda$$

$$f(N) = c\exp\left(-\lambda N\right)$$

eigenvalue equation $\Rightarrow$

$$-\frac{b^2}{6}\Delta\psi(\vec{R}) + \frac{\varphi(\vec{R})}{k_B T}\psi(\vec{R}) = \lambda\psi(\vec{R})$$

eigenvalues λ_{n}, complete set (orthogonal) eigenfunctions $\psi_{\mathrm{n}}(\vec{R})$

$$G = \psi_n(\vec{R})\exp\left(-\lambda_n N\right)$$

or any linear combination for different n

A polymer in an external field (3)

linear combination: $G_N(\vec{R}\,|\,\vec{R}') = \sum_n c_n \psi_n(\vec{R}) \exp\left(-\lambda_n N\right)$

using $\vec{R} \leftrightarrow \vec{R}'$

bilinear expansion: $G_N(\vec{R}\,|\,\vec{R}') = \sum_n \psi_n(\vec{R}) \psi_n(\vec{R}') \exp\left(-\lambda_n N\right)$

where $-\frac{b^2}{6}\Delta\psi_n(\vec{R}) + \frac{\varphi(\vec{R})}{k_B T}\psi_n(\vec{R}) = \lambda_n \psi_n(\vec{R})$

1) continuous spectrum of eigenvalues

example: $\varphi(\vec{R}) = 0 \quad \Rightarrow \quad \psi_{\vec{k}} = e^{i\vec{k}\bullet\vec{R}}$ and $\lambda_{\vec{k}} = \frac{1}{6} b^2 k^2$

here we need all eigenfunctions $\Rightarrow$ Gaussian coil

A polymer in an external field (4)

bilinear expansion: $G_N(\vec{R}\,|\,\vec{R}') = \sum_n \psi_n(\vec{R})\psi_n(\vec{R}')\exp\left(-\lambda_n N\right)$

2) discrete spectrum of eigenvalues

$\Rightarrow$ lowest eigenvalue λ_0 dominates for large N

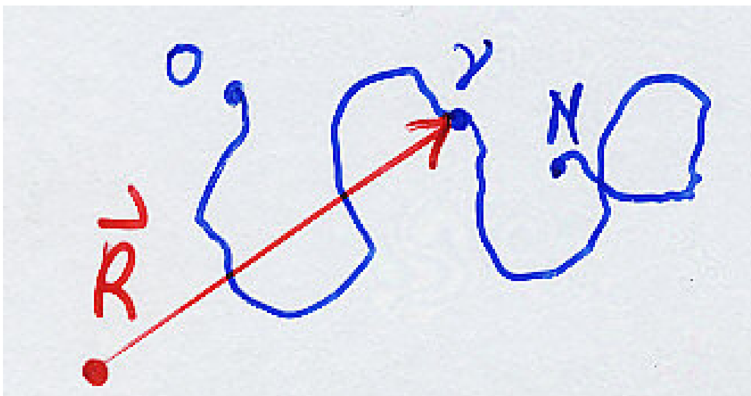
GROUND STATE DOMINANCE

$$G_N(\vec{R}\,|\,\vec{R}') \sim \psi_0(\vec{R})\psi_0(\vec{R}')\exp\left(-\lambda_0 N\right)$$

chain ends are decoupled!

A polymer in an external field (5)

segment density $c(\vec{R})$?



integrate over: beginning

end

ν

$$c(\vec{R}) \sim N\left|\psi_0\left(\vec{R}\right)\right|^2$$ cf. QM: bound state

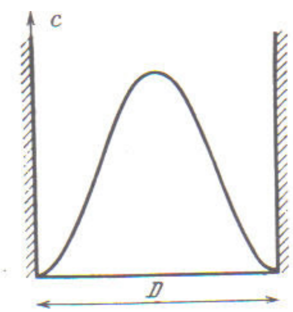
A polymer in an external field (6)

Figure 5. A polymer chain in a spherical cavity of diameter D.

An example of this situation is a polymer chain confined to a spherical cavity of diameter D (see figure 5). For this spherical symmetry we can express the Laplacian in terms of the distance to the origin R:

$$\Delta \cdots = \frac{1}{R}\frac{d^2}{dR^2}(R\cdots)$$

If we now solve equation (2.16) with $\varphi(\mathbf{R}) = 0$ within the cavity, but all eigenfunctions $= 0$ outside (since the chain obviously cannot be there), we find as the lowest eigenvalue and (normalized) eigenfunction:



Segment density of a very long ideal polymer in a spherical cavity of diameter D.

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$$\lambda_0 = \frac{2\pi^2 b^2}{3D^2} \text{ and } \psi_0 = \frac{1}{R\sqrt{\pi D}}\sin\left(\frac{2\pi R}{D}\right)$$

Lifshitz entropy: derivation

(for ground-state dominance)

Partition function Z: # conformations

(weighed with Boltzmann factors $\exp(-\varphi(\vec{R})/k_B T)$)

$$Z = \int d\vec{R} \int d\vec{R}' G_N(\vec{R} \mid \vec{R}')$$

$$G_N(\vec{R} \mid \vec{R}') \sim \psi_0(\vec{R})\psi_0(\vec{R}')\exp(-\lambda_0 N)$$

$$Z \sim e^{\lambda_0 N} \left(\int d\vec{R}\, \psi_0(\vec{R}) \right)^2$$

end effects

free energy:

$$A = -k_B T \ln Z \sim k_B T \lambda_0 N + \text{end effects}$$

entropy:

$$S = \frac{U - A}{T} = \int \frac{1}{T} \varphi(\vec{R}) c(\vec{R})\, d\vec{R} - k_B \lambda_0 N$$

use $c(\vec{R}) \sim N{\psi_0}^2$

and the eigenvalue equation

and eliminate λ_0

Lifshitz entropy: result

$$S = Nk_B \frac{1}{6} b^2 \int \psi_0(\vec{R}) \Delta \psi_0(\vec{R})\, d\vec{R}$$

$$S = -Nk_B \frac{1}{6} b^2 \int \left[\vec{\nabla} \psi_0(\vec{R}) \right]^2 d\vec{R}$$ partial integration using $\Delta \equiv \vec{\nabla} \bullet \vec{\nabla}$

$$S = -k_B \frac{1}{24} b^2 \int \frac{[\vec{\nabla} c(\vec{R})]^2}{c(\vec{R})} d\vec{R}$$ using $c(\vec{R}) \sim N\psi_0{}^2$

- independent of $\varphi(\vec{R})$
- also valid for a collection of polymers
- S decreases because of concentration gradients
- $S = S[c(\vec{R})]$ (S is a functional of $c(\vec{R})$)

Self-consistent field method

this method incorporates inter-segment interactions:

free energy:

$$A[c(\vec{R})] = U[c(\vec{R})] - TS[c(\vec{R})]$$

$U[c(\vec{R})]$ represents e.g. a non-ideal gas of segments

$c_{eq}(\vec{R})$ is then obtained by functional minimization

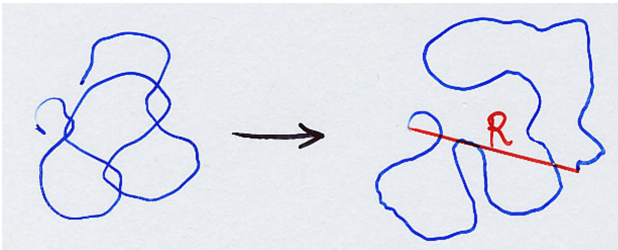
THIS APPROACH NEGLECTS FLUCTUATIONS/CORRELATIONS !

Non-ideal polymer chains

$$U[c(\vec{R})] = Nk_B TB\, c(\vec{R})$$

B is the second virial coefficient ($B > 0$ repulsion)

Edwards (1965): $\left\langle \vec{R}^2 \right\rangle \propto N^{6/5}$



swelling
PURE REPULSION

total number of configurations (depending on R) $\propto$

$$\propto P(R,N) \propto 4\pi R^2 \exp\left(-\frac{3R^2}{2Nb^2}\right)$$

but a certain fraction of these configurations is "forbidden":

$$p(R) \approx \left(1 - \frac{v_c}{R^3}\right)^{N(N-1)/2} \approx \exp\left(-\frac{N^2 v_c}{2R^3}\right)$$

Non-ideal (repulsive) polymer chains

free energy:

$$\frac{A(R)}{k_B T} = -\frac{S(R)}{k_B T} = -\ln\left[p(R)P(R,N)\right]$$

$$\approx \text{cst} - 2\ln R + \frac{3R^2}{2Nb^2} + \frac{N^2 v_c}{2R^3}$$

minimize $A(R)$ with respect to R

$$v_c = 0: \quad R_0^* \propto N^{1/2} b$$

$$v_c \neq 0: \quad \left(\frac{R^*}{R_0^*}\right)^5 - \left(\frac{R^*}{R_0^*}\right)^3 \approx \frac{v_c}{b^3} N^{1/2} \quad \text{Flory}$$

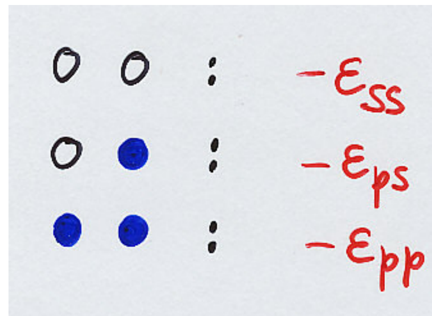
$$N \gg 1: \quad R^* \approx R_0^* N^{1/10} \propto N^{3/5} b \quad \text{SWELLING !}$$

$$\text{RG theory / simulations}: \quad R^* \propto N^{0.588} b$$

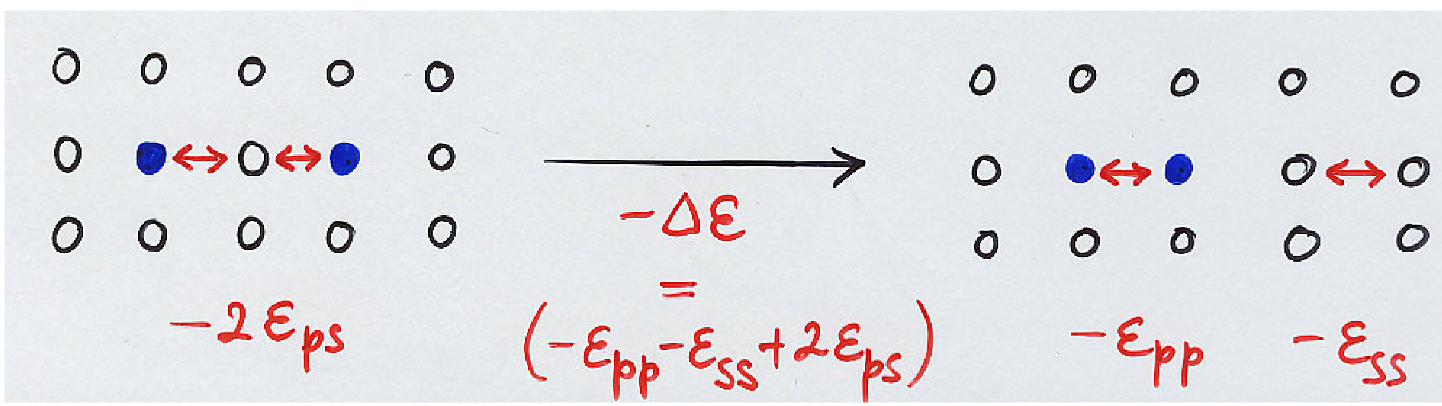
Repulsion combined with attraction (1)

Assumptions:

- only attraction between nearest neighbours
- coordination number: z
- solvent-solvent
  solvent-polymer
  polymer-polymer



- random **pair** contacts:



Repulsion combined with attraction (2)

attractive energy within a coil:

$$U_{attr} = N\nu_c \, c(R) \, z \, (-\Delta\varepsilon)$$

($\nu_c \, c(R)$ is the probability to find a neighbouring segment)

$$\frac{U_{attr}}{k_B T} = -\frac{N^2}{R^3}\nu_c \frac{z\Delta\varepsilon}{k_B T}$$ where $\frac{z\Delta\varepsilon}{k_B T} \equiv \chi$ (chi-parameter)

χ usually > 0

Compare with repulsive term in $\frac{A(R)}{k_B T}$, which was: $\frac{N^2 \nu_c}{2R^3}$

$$\nu_c \rightarrow \nu \equiv \nu_c \left(1 - 2\chi\right)$$

$$\left(\frac{R^*}{R_0^*}\right)^5 - \left(\frac{R^*}{R_0^*}\right)^3 \approx \frac{\nu_c}{b^3}\left(1 - 2\chi\right) N^{1/2}$$ Flory

Repulsion combined with attraction (3)

$$\left(\frac{R^*}{R_0^*}\right)^5 - \left(\frac{R^*}{R_0^*}\right)^3 \approx \frac{v_c}{b^3}(1-2\chi)\,N^{1/2} \quad \text{Flory}$$

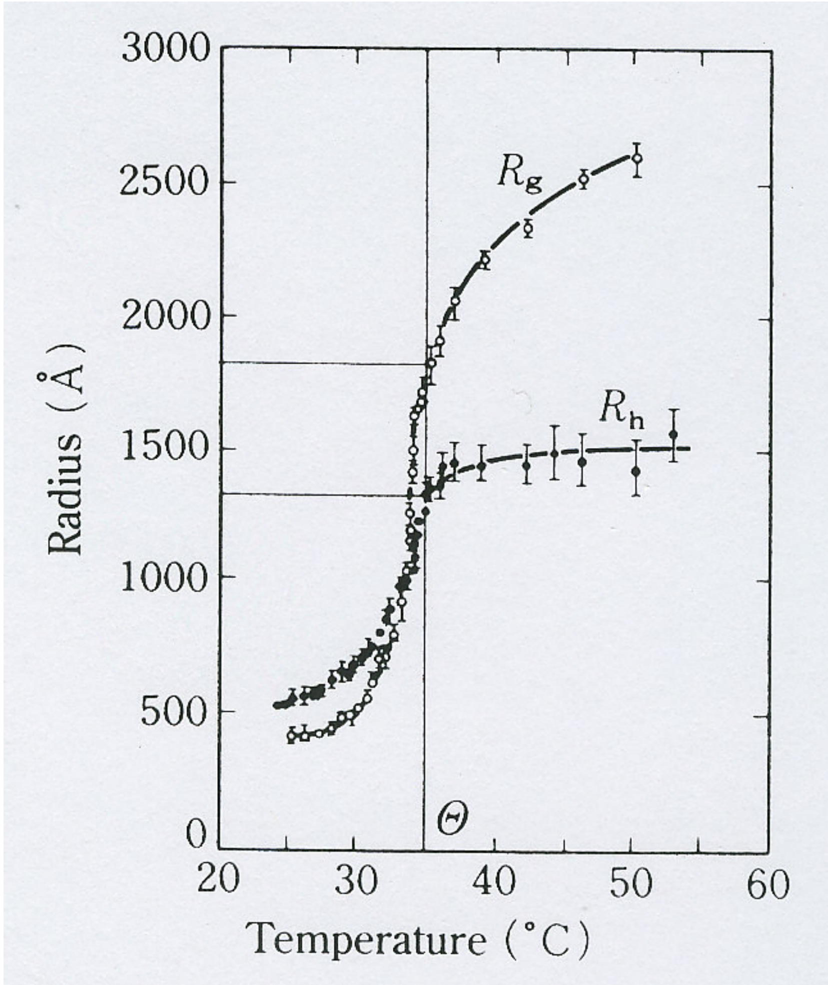
CONCLUSION:

- at $\chi = 0$ swollen chain $R^* \propto N^{3/5}$
- at $\chi = 1/2$ (θ - temperature): ideal chain $R^* = R_0^* \propto N^{1/2}$
- right-hand side only small if $\chi = \frac{1}{2} - \frac{\text{cst}}{\sqrt{N}}$ i.e. abrupt change if N large

$\chi > 1/2$: globule (bound state, cf. QM) $R^* \propto N^{1/3}$

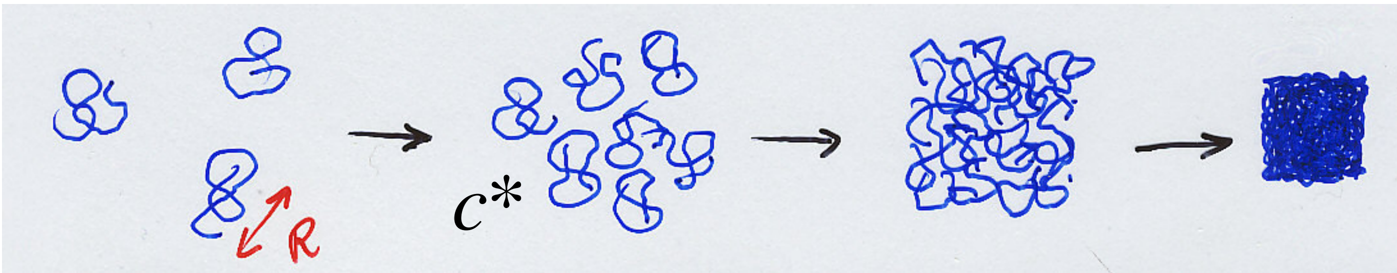
- in general $R^* \sim b\, N^{\nu}$

Repulsion combined with attraction (4)



polystyrene in cyclohexane

Concentrated polymer solutions



$$c^* \approx \frac{N}{R^3} \approx \frac{N}{(bN^\nu)^3} \approx \frac{\left(N^{-1/2} \leftrightarrow N^{-4/5}\right)}{b^3} \quad \text{very small !}$$

FLORY-HUGGINS:

- concentrated systems: $S(\vec{R})$ NO
- homogeneous systems: S_{Lifshitz} NO
- random mixing (Ω places) YES

Flory-Huggins theory (1)

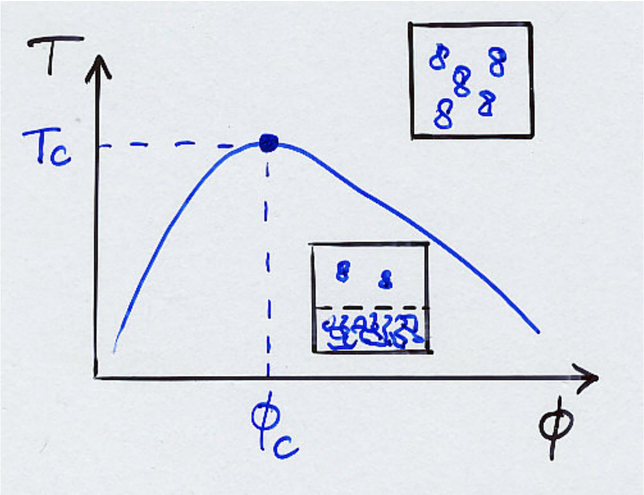
translational entropy: $S_{tr,sp} \approx -k_B \Omega_{sp} \ln \phi_{sp} \quad (sp = \text{species})$

polymer: $A_{m,p} \approx k_B T \Omega \dfrac{\phi}{N} \ln \phi$

solvent: $A_{m,s} \approx k_B T \Omega (1-\phi) \ln(1-\phi)$

$$A_m \approx \Omega k_B T \left[\frac{1}{N} \phi \ln \phi + (1-\phi)\ln(1-\phi) + \chi \phi (1-\phi) \right]$$

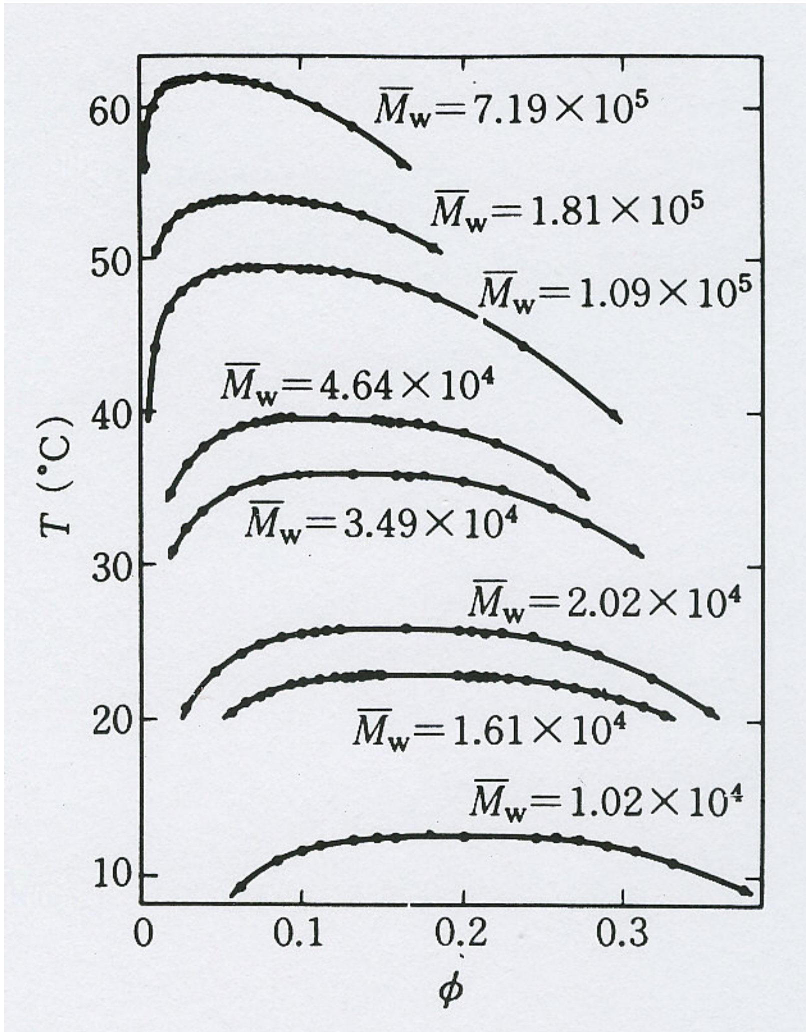
Flory-Huggins theory (2)



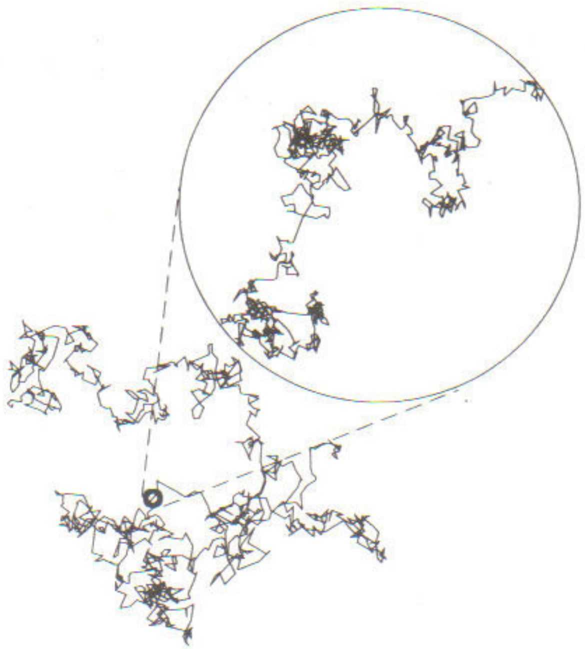
- $\phi_c = \dfrac{1}{1+\sqrt{N}}$ (highly) asymmetric
- T_c follows from $\chi_c \approx \dfrac{1}{2} + \dfrac{1}{\sqrt{N}}$

  $T_c \to \theta$ for large N, i.e. near the coil $\to$ globule transition
- note that fluctuations are neglected!

Polystyrene in methylcyclohexane



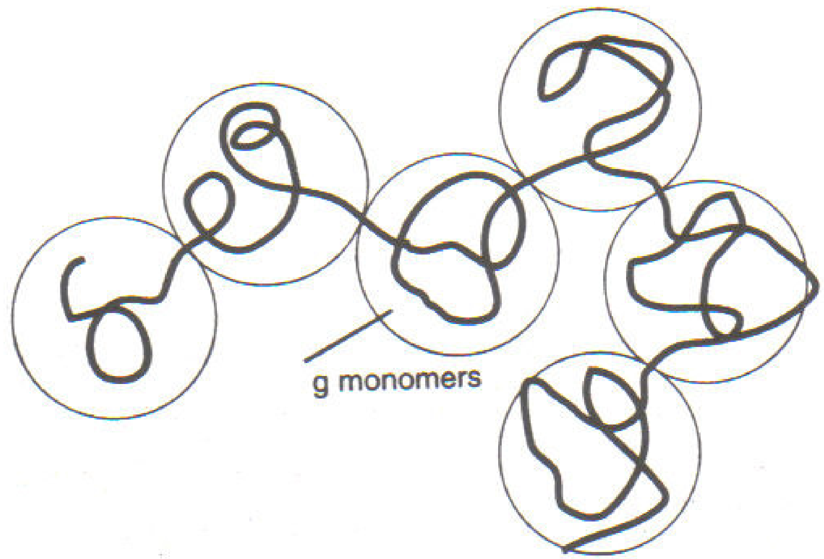
Scaling theory



step length : $b \longrightarrow b_g \left(\equiv g^{1/2} b\right)$

number : $N \longrightarrow N_g \ (\equiv N/g)$

end–to–end distance : $N^{1/2} b \longrightarrow N_g^{1/2} b_g \left(= N^{1/2} b\right)$ invariant!



Semi-dilute solution (good solvent)

$$\phi^* \approx b^3 c^* \approx b^3 \frac{N}{(bN^{3/5})^3} \approx N^{-4/5}$$ still very small !

OSMOTIC PRESSURE

TYPICAL LENGTH SCALE

DILUTE

$$\Pi = k_B T \frac{c}{N}$$

$$\xi (= R) = bN^{3/5}$$

SEMI-DILUTE
(power law)

$$\Pi \sim k_B T \frac{c}{N}\left(\frac{\phi}{\phi^*}\right)^m$$

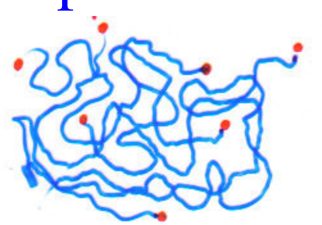
$$\xi \sim bN^{3/5}\left(\frac{\phi}{\phi^*}\right)^m$$

$$\sim k_B T \frac{c}{N^1} N^{4/5m} \phi^m$$

independent of N

$$\sim bN^{3/5} N^{4/5m} \phi^m$$

$m = 5/4$



$m = -3/4$

$$\Pi \sim k_B T c\,\phi^{5/4} \sim \frac{k_B T}{b^3}\phi^{9/4}$$

$$\xi \sim b\,\phi^{-3/4}$$

des Cloizeaux

de Gennes

What is the meaning of ksi ? (1)

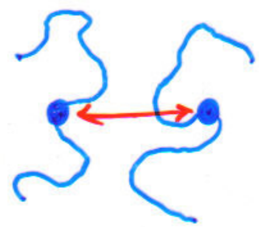
Flory-Huggins: $\Pi \sim \frac{k_B T}{b^3}\phi^{2} \sim \frac{k_B T}{b^3}\phi \times \phi$

des Cloizeaux: $\Pi \sim \frac{k_B T}{b^3}\phi^{9/4} \sim \frac{k_B T}{b^3}\phi \times \phi^{5/4}$

probability of segment $\times$ probability of contact w

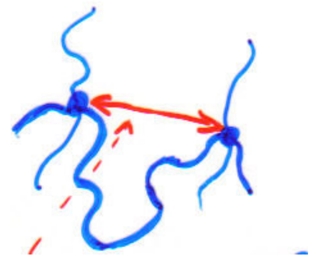
probability of contact w: **lower** for scaling theory (correlations!)

Flory-Huggins: 

des Cloizeaux: 

What is the meaning of ksi ? (2)

on one chain: number of segments between contacts?



g monomers: $g \sim w^{-1} \sim \phi^{-5/4}$

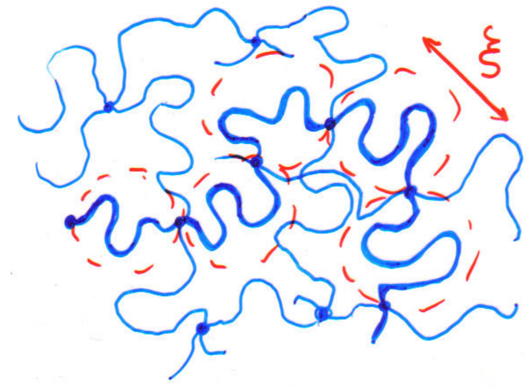
$$bg^{3/5} \sim b\left(\phi^{-5/4}\right)^{3/5} \sim b\phi^{-3/4} \sim \xi$$ distance between chain contacts !

1) volume fraction within one blob:

$$\frac{gb^3}{\xi^3} \sim \frac{\phi^{-5/4}b^3}{(b\phi^{-3/4})^3} \sim \phi \quad \Rightarrow$$ blobs touch !

What is the meaning of ksi ? (3)

2) a SEMI-DILUTE SOLUTION
is a collection of BLOBS !



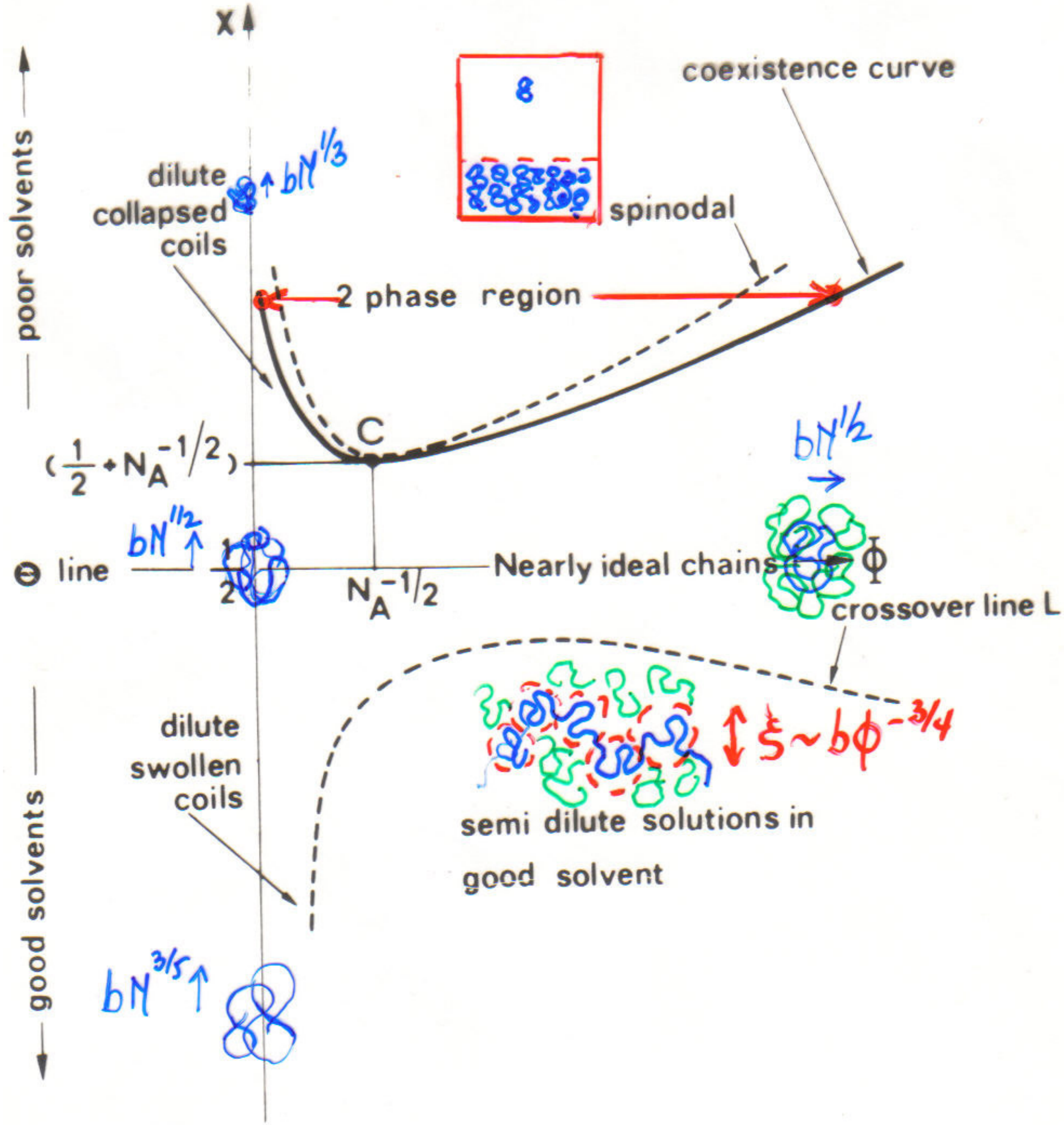
de Gennes: $\xi \sim b\phi^{-3/4}$

3) des Cloizeaux: $\Pi \sim \frac{k_B T}{b^3}\phi^{9/4} \sim \frac{k_B T}{\xi^3}$ blobs are the osmotic units

4) ξ is also the screening length for the excluded volume

5) $\phi \to 1: \quad \xi(\sim b\phi^{-3/4}) \to b$

chains in polymer melts are ideal! (Flory)



χ
poor solvents
good solvents
dilute collapsed coils
$bN^{1/3}$
coexistence curve
spinodal
2 phase region
C
$(\frac{1}{2} + N_A^{-1/2})$
$bN^{1/2}$
Θ line
$\frac{1}{2}$
$N_A^{-1/2}$
Nearly ideal chains
Φ
crossover line L
$\xi \sim b\phi^{-3/4}$
dilute swollen coils
semi dilute solutions in good solvent
$bN^{3/5}$