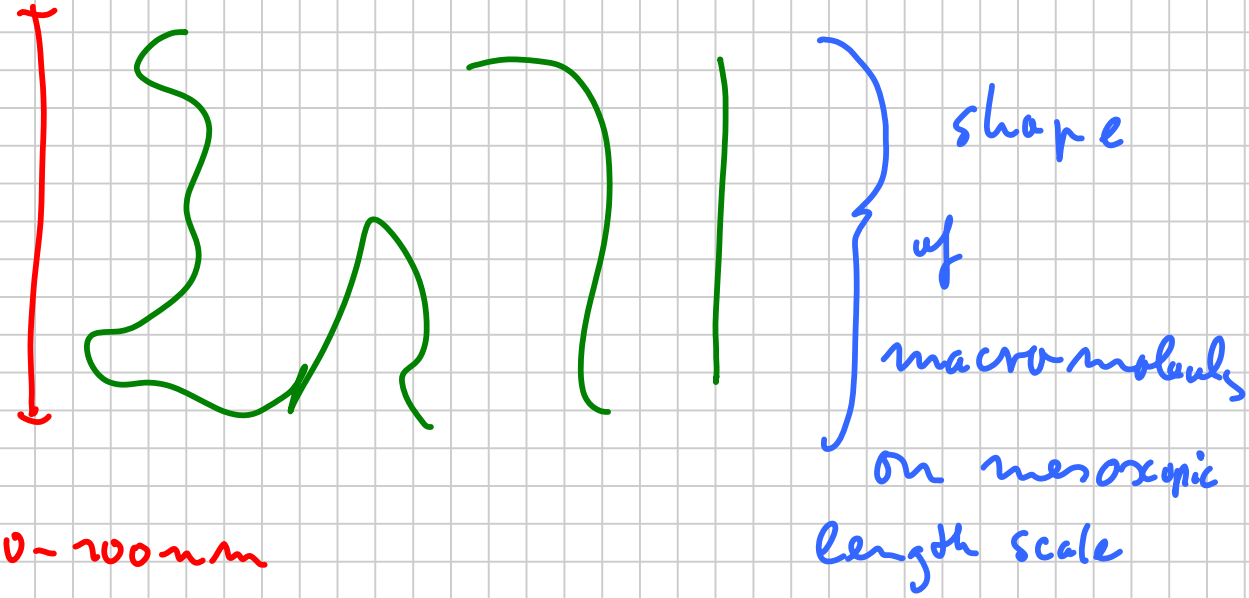
3. Macromolecules in solution



- interaction with solvent
- shape, stiffness
- concentrated solution
- → networks

Analysis of solution

(2D : 3R)

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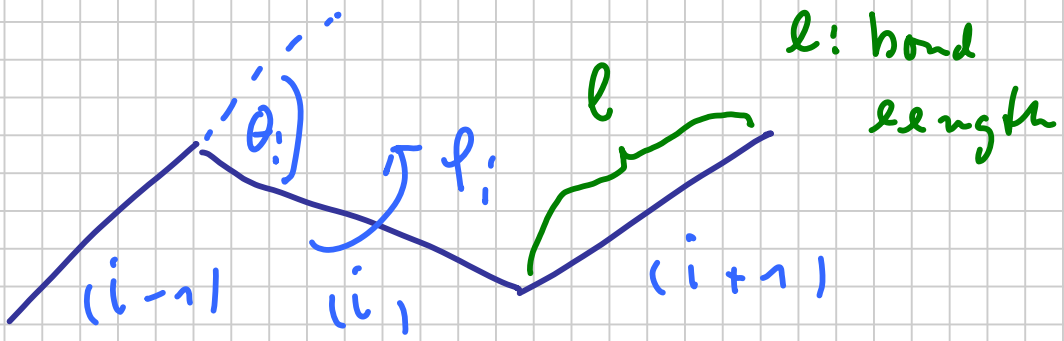
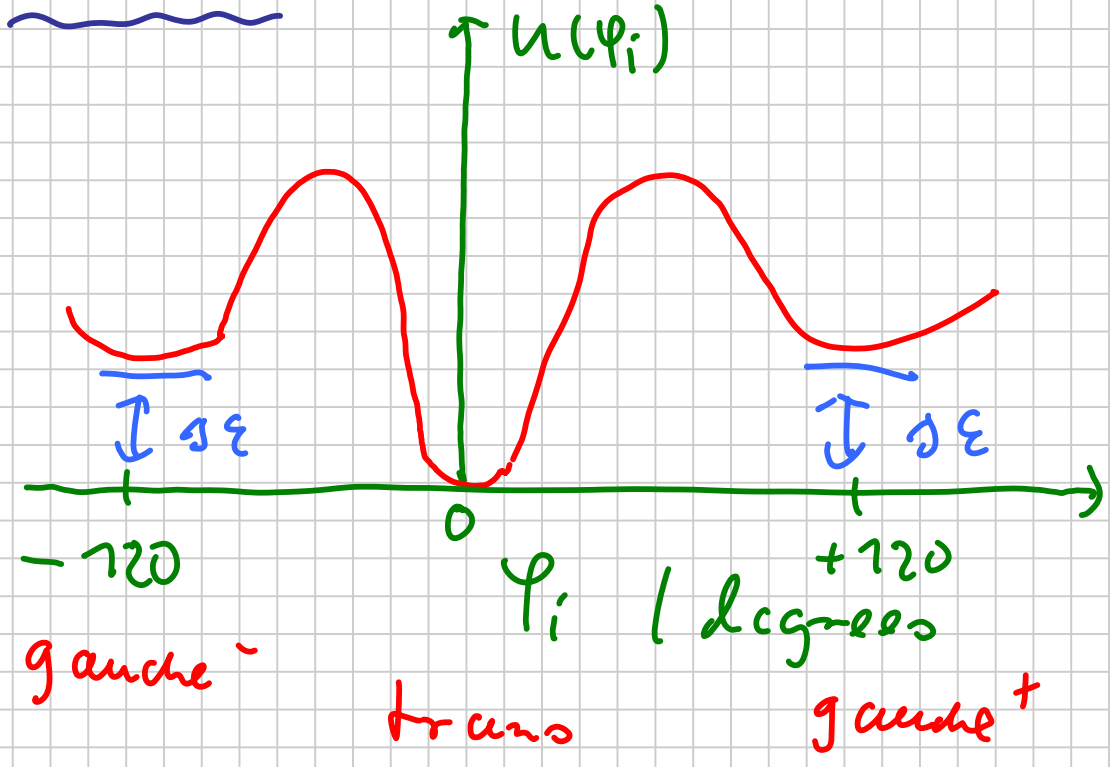
Rubinstein / Colby
Chapter 2



θ_i : bond angle : fixed

φ_i : torsional angle : assumes certain values

Alkanes:



Assumption: Conf. energy of
given bond depends only
on next neighbours

⇒ solution by

Rotational isomeric state model
(RIS) Volkenstein, Flory

⇒ 1D Ising model but with
3 different states

... ↑↓↑↑↓↓↓ ...

exact solution known

⇒ RIS can be solved exactly
but too tedious for practical
purposes

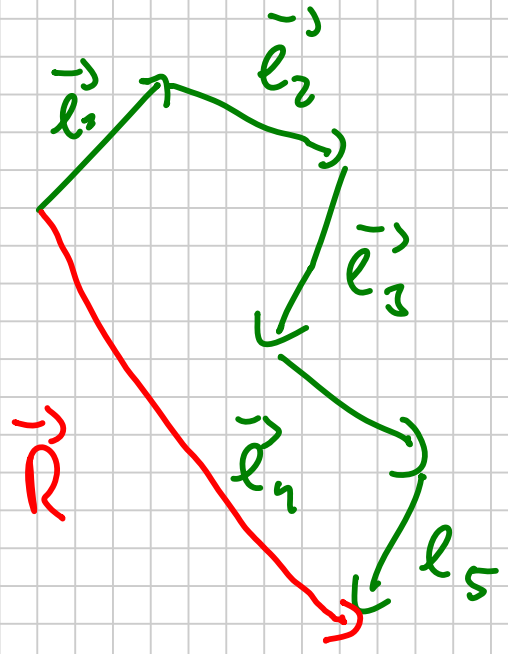
Freely rotating chain:

Θ: fixed ; φ: free

still too complicated for many purposes

Freely jointed chain:

Θ: free φ: free l: fixed



$\vec{l}_i$: bond vector

$\vec{R}$: end-to-end vector

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Suitable model for polymers:

$$\vec{R} = \sum_i^n \vec{e}_i$$

direct application of random walk model

$\langle \dots \rangle$ ensemble average

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

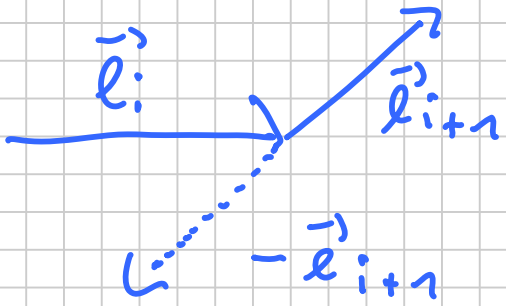
since random walk has no defined direction (→ diffusion

$$\langle R^2 \rangle = \langle \vec{R}^2 \rangle = \langle \vec{R}\,\vec{R} \rangle =$$

$$\left(\sum_i \vec{r}_i \right) \left(\sum_j \vec{r}_j \right) = \sum_{i,j} \langle \vec{r}_i\, \vec{r}_j \rangle$$

$$\vec{r}_i\, \vec{r}_j = l^2 \cos\Theta$$

$$\langle \cos\theta \rangle = 0$$



same probability

$$\langle R^2 \rangle = \sum_i l^2 = n l^2$$

$$\langle R^2 \rangle^{\frac{1}{2}} \sim \sqrt{n}$$

Scaling law

$\Rightarrow$ diffusion

Coarse model but correct

Scaling law :

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It can be shown that the freely rotating chain leads to

$$\langle R^2 \rangle = n l^2 \frac{1 + \cos\theta}{1 - \cos\theta}$$

Alkanes: $\theta = 68°$

$$\frac{1 + \cos\theta}{1 - \cos\theta} = 2$$

in general:

$$\langle R^2 \rangle = C_\infty n l^2$$

C_∞: characteristic ratio for chain of infinite length

C_n: ... for chain with n segments

⇒ different models lead to same scaling law

$$\langle R^2 \rangle \sim n$$

molecular details as e.g. bond angles are meshed into single parameter C_∞ ⇒

Scaling laws are independent of molecular details.

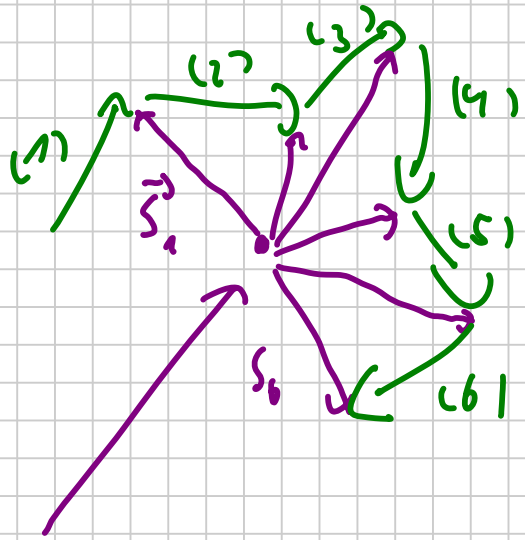
Polymers ⟷ Diffusion

$\langle R^2 \rangle \sim n$ $\quad$ $\langle \Delta x^2 \rangle \sim t$

n: chain length $\quad$ t: time

different problems but same stat. mech. model: random walk

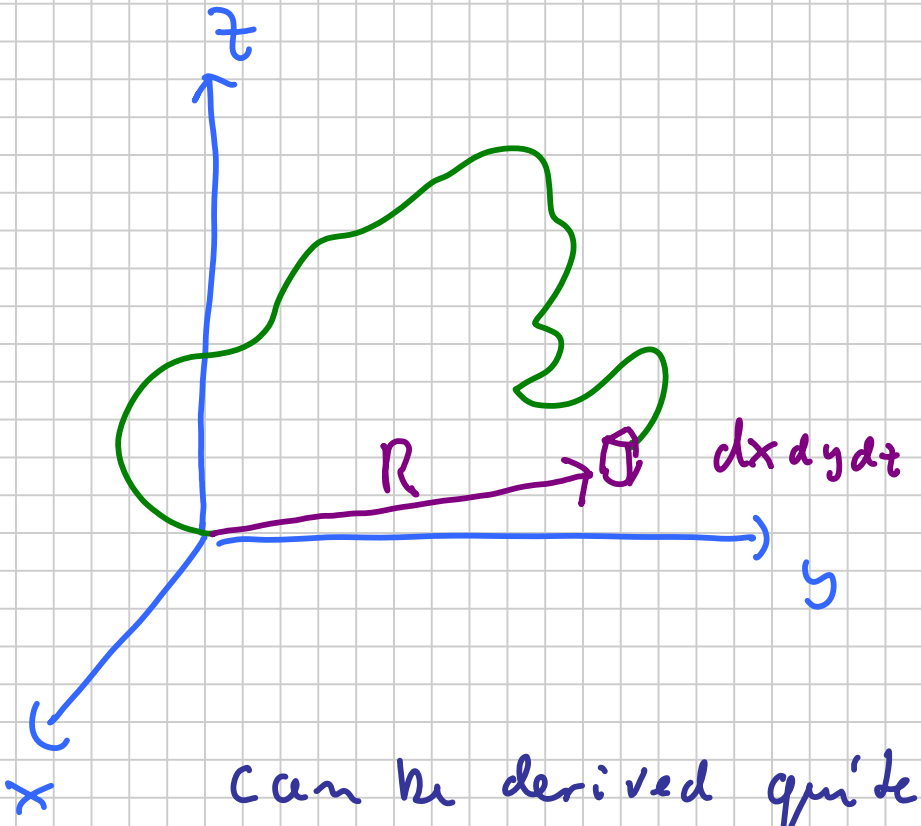
Important exp'l quantity:
radius of gyration $\langle s^2 \rangle$



$$\langle s^2 \rangle = \frac{1}{n} \left(\sum_i s_i^2 \right) \xrightarrow{\text{Lagrange}}$$

$$\langle s^2 \rangle = \frac{1}{n^2} \sum_{j \le \lambda \le n} r_{ik}^2$$

3D distribution $W(\vec{r})\,d\vec{r}$



can be derived quite easily:

$$W(R) = W(x)\,W(y)\,W(z)$$

Since 3 directions are stat. independent

$$W(\vec{R}) = W(-\vec{R}) \hat{=} W(R)$$

Since W can be a function only of scalar property

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$$R^2 = x^2 + y^2 + z^2$$

$$W(R^2) = W(x^2)\, W(y^2)\, W(z^2)$$

Only Gaussian fulfils this Condition

$$W(x^2) \sim \exp\left[-a x^2\right]$$

$$W(R^2) = \text{const} \exp\left[-c R^2\right]$$

Normalization

$$\int W(R^2)\, dx\, dy\, dz = 1$$

and

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$$\langle R^2 \rangle = \frac{\int R^2 W(R^2)\, dx\, dy\, dz}{\int W(R^2)\, dx\, dy\, dz} = nl^2$$

$$W(R^2)\, dx\, dy\, dz = \left(\frac{\beta}{\sqrt{\pi}}\right)^3 e^{-\beta^2 R^2} dx\, dy\, dz$$

$$= \left(\frac{\beta}{\sqrt{\pi}}\right)^3 e^{-\beta^2 R^2} 4\pi R^2\, dR$$

because of spherical symmetry of problem

Vergleich mit Experiment:

$$C_n = \frac{\langle R^2 \rangle}{n l^2}$$

oder lim $n \to \infty$ $C_n \to C_\infty$

"equivalent chain"

real chain	Kuhn-chain
n : segments	n' segments
l : bond length	l_K Kuhn length

$$n \cdot l = r_{max} = n' l_K$$

$$n' l_K^2 = \langle R^2 \rangle$$

$\rightarrow$ n', l_K from exp'l data

e.g. Polyethylene $-CH_2-CH_2-$

$$\langle R^2 \rangle = 6.7\, n l^2$$

$\Rightarrow$

$$\frac{n}{n'} = 10$$

$\sim$ approximately 10 C-C-bonds constitute one Kuhn segment

Mesoscopic range: all atomistic details are mapped on single length parameter l_K $\Rightarrow$ sufficient description of physics of chains

Important consequence: chain only determined by its entropy

Extension of chain by external force

Boltzmann $S = k \ln W$

Kuhn chain

$$W(R^2)\, dV = \left(\frac{\beta}{\sqrt{\pi}}\right)^3 e^{-\beta^2 R^2}\, dV$$

$$\beta^2 = \frac{3}{2nl^2}$$

Entropy of chain

$$S = \text{const} - k\beta^2 R^2 =$$

$$= \text{const} - k \frac{3R^2}{2nl^2}$$

In general force f is given by

L: extension

$$f = \left(\frac{\partial F}{\partial L}\right)_{T,V} \qquad F(T,V,L)$$

because of

$$dF = -S\,dT - p\,dV + f\,dL$$

f, L : conjugated variables

Therefore

$$f = \left(\frac{\partial U}{\partial L}\right)_{T,V} - T\left(\frac{\partial S}{\partial L}\right)_{T,V}$$

$$\| \quad 0$$

by definition

$$f = -T\left(\frac{\partial S}{\partial L}\right)_{T,V}$$

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$L \to R$

$$f = 3RT \frac{R}{\langle R^2 \rangle}$$

for small extensions

Discussion 1) $W(R')$ has maximum at $R = 0$ $\Rightarrow$ most probable state $\to$ small perturbation / extension $\to$ $S \uparrow \Rightarrow f \uparrow$

2) $\left(\frac{\partial F}{\partial T}\right)_{V,L} = -S \qquad \left(\frac{\partial F}{\partial L}\right)_{V,T} = f$

$$\left(\frac{\partial^2 F}{\partial T \partial L}\right) = \left(\frac{\partial^2 F}{\partial L \partial T}\right) \Rightarrow$$

$$-\left(\frac{\partial S}{\partial L}\right)_{T,V} = \left(\frac{\partial f}{\partial T}\right)_{V,L} > 0$$

Force increases with temperature

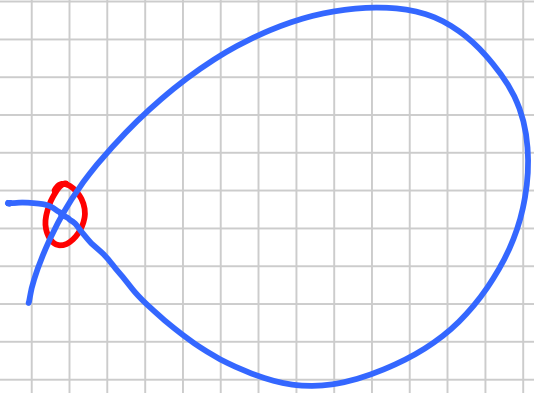
Entropy elasticity

is opposite to energy elasticity

where $\left(\frac{\partial f}{\partial T}\right) < 0$

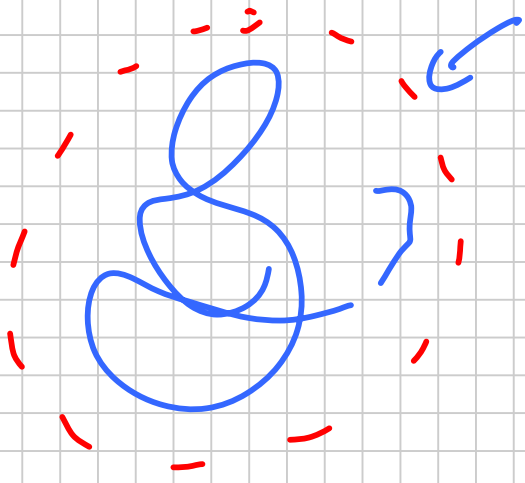
⇒ Extension to ensemble of many chains: Theory of rubber elasticity

Up to now "unperturbed chain" random walk can cross its own path



forbidden in real system

Why is this important?



volume of coil V_{coil}

volume fraction of segments ϕ

$$\phi = \frac{n\, V_{segment}}{V_{coil}}$$

$\phi \sim 0.01$ => enough space for subsequent segments

However: probability for finding free space for new segment:

$$\sim 1 - \phi \sim 0.99 \sim 1$$

But: we need to introduce n segments ($n \geq 100$)

$$\sim (1-\phi)^n \sim 0.99^{100} \sim 0.3$$

for n of sufficient magnitude

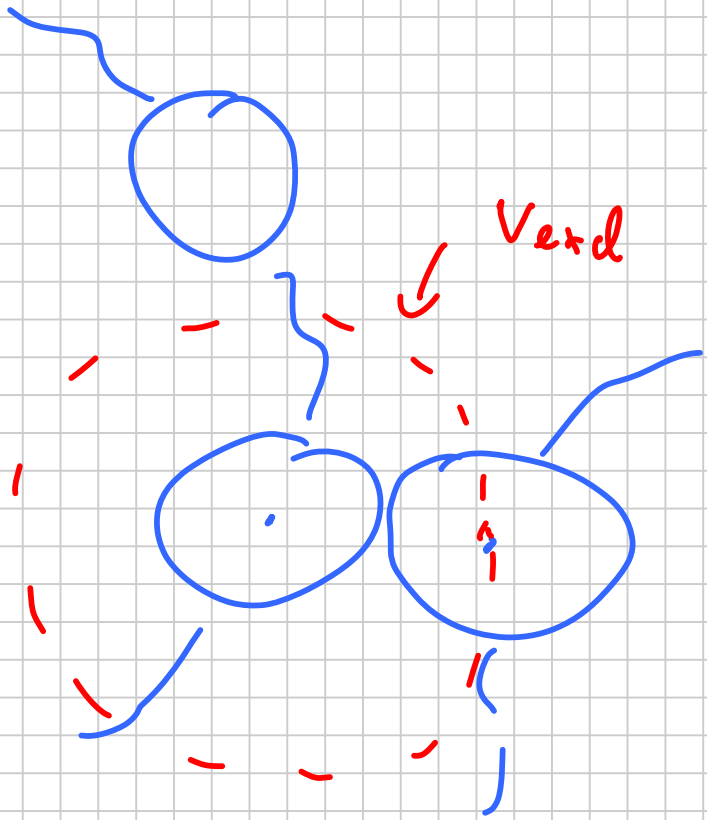
$$(1-\phi)^n \to 0$$

Extended Volume problem

Therefore: coil expands to ease this problem

$$\langle R^2 \rangle = \alpha^2 \langle R_0^2 \rangle$$

↑ unperturbed dimensions for Gaussian stat.



A simple model leads to quantitative treatment (Flory, de Gennes)

N: number of segments

R: linear dimensions of coil

Segment concentration c

$$c \sim \frac{N}{R^3}$$

free energy of repulsion F_{rep} per pair of segments

$$F_{rep} \sim kT\, v_{excl} \cdot c^2$$

$$\sim kT\, v_{excl}\, \frac{N^2}{R^6}$$

Integration of all pairs

$$F_{rep,tot} \sim f_{rep} \cdot R^3 =$$

$$= V_{excl} \frac{N^2}{R^3}$$

⇒ will expand coil

retracting force

$$f_{el} \sim k_B T \frac{R^2}{N l^2}$$

$$F = F_{rep,tot} + f_{el} =$$

$$= V_{excl} \frac{N^2}{R^3} + \frac{R^2}{N l^2}$$

Minimum at $\left(\frac{\partial F}{\partial R}\right)_T = 0$

$$0 = -v_{ex} d \frac{N^2}{R^4} + 2 \frac{R}{N\ell^2}$$

$$R \sim N^{\frac{3}{5}} \sim N^{\nu}$$

ν : Flory exponent

$$\nu = \frac{3}{d+2}$$

d: dimension of space

$d = 4 \Rightarrow \nu = \frac{1}{2}$: Gaussian stat.

$\Rightarrow$ no problem !

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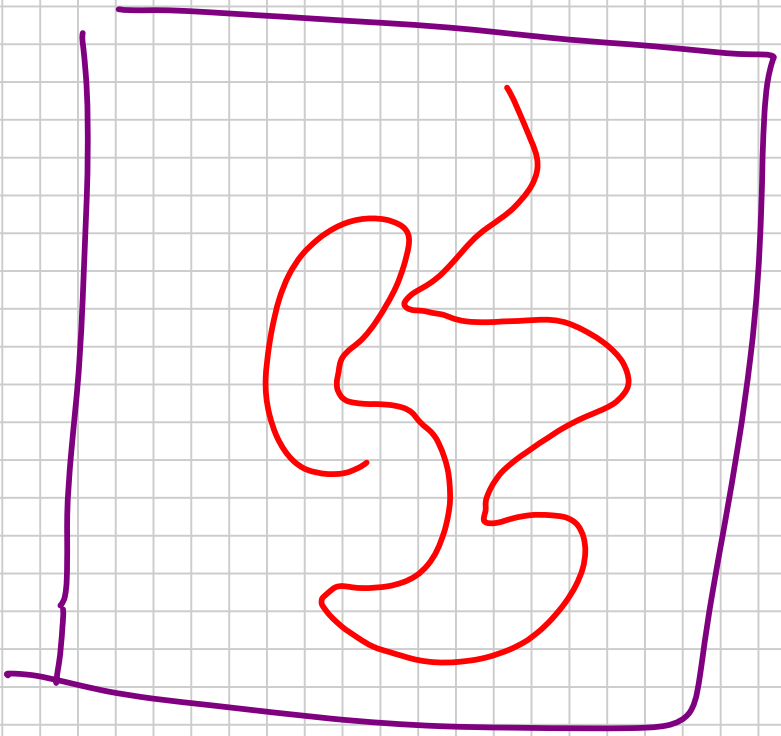
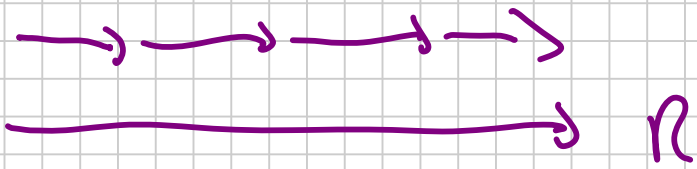
$d = 2$ $\quad \nu = \frac{3}{4}$ $\Rightarrow$

much stronger than in 3D

$\Rightarrow$ polymers on surfaces



$d = 1$ $\quad \nu = 1$ $\quad R \sim N$



Solution : Unperturbed dimensions can be reached at

$$T = \Theta$$

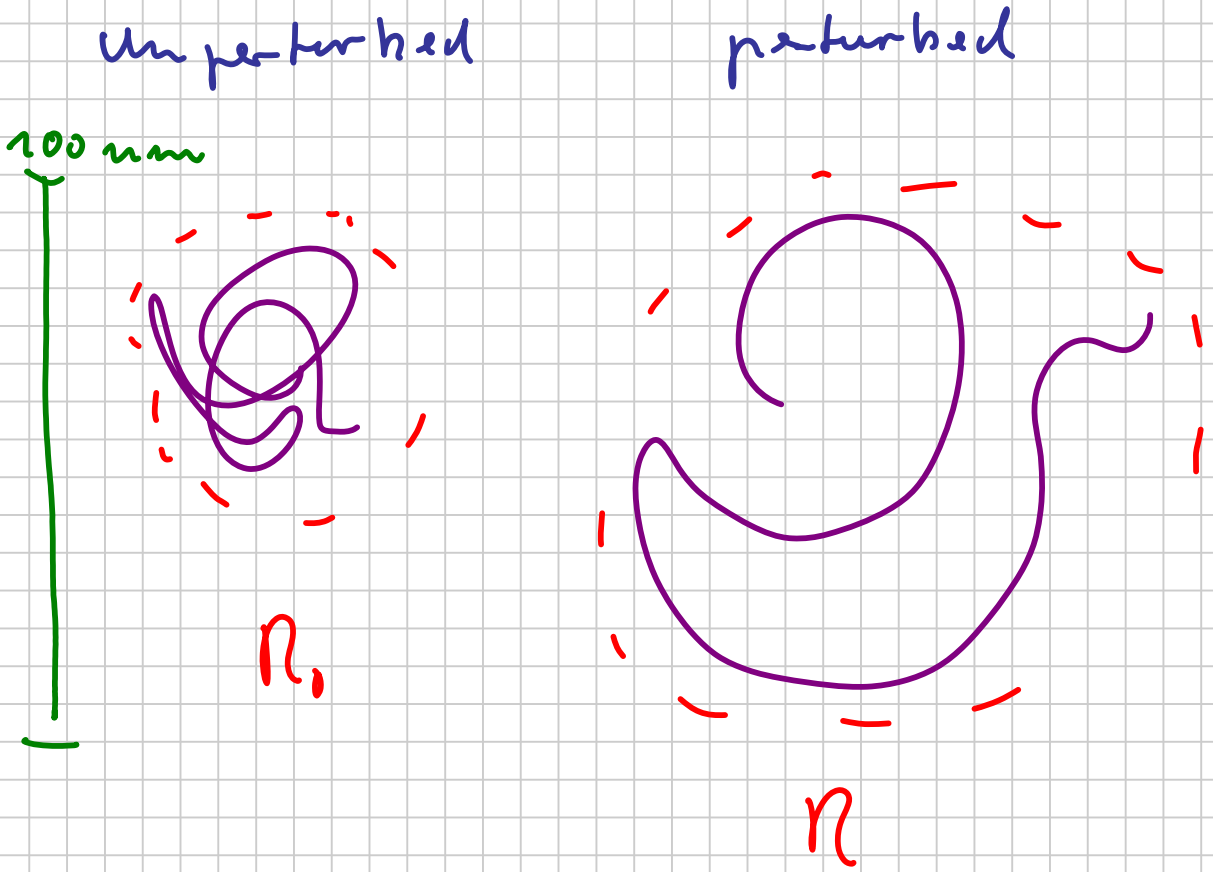
Θ : theta - temperature (Flory)

$$V_{excl} \sim b - \frac{a}{RT}$$

$$\sim \left(1 - \frac{\Theta}{T}\right)$$

$V_{excl} = 0$ at $T = \Theta$ => effect of excluded volume balanced by attractive interaction

But : Only on mesoscopic length scale !



$$\langle R^2 \rangle = \alpha^2 \langle R_0^2 \rangle$$

effect in mesoscopic dimensions

can be mapped on V_{excl}, ☺

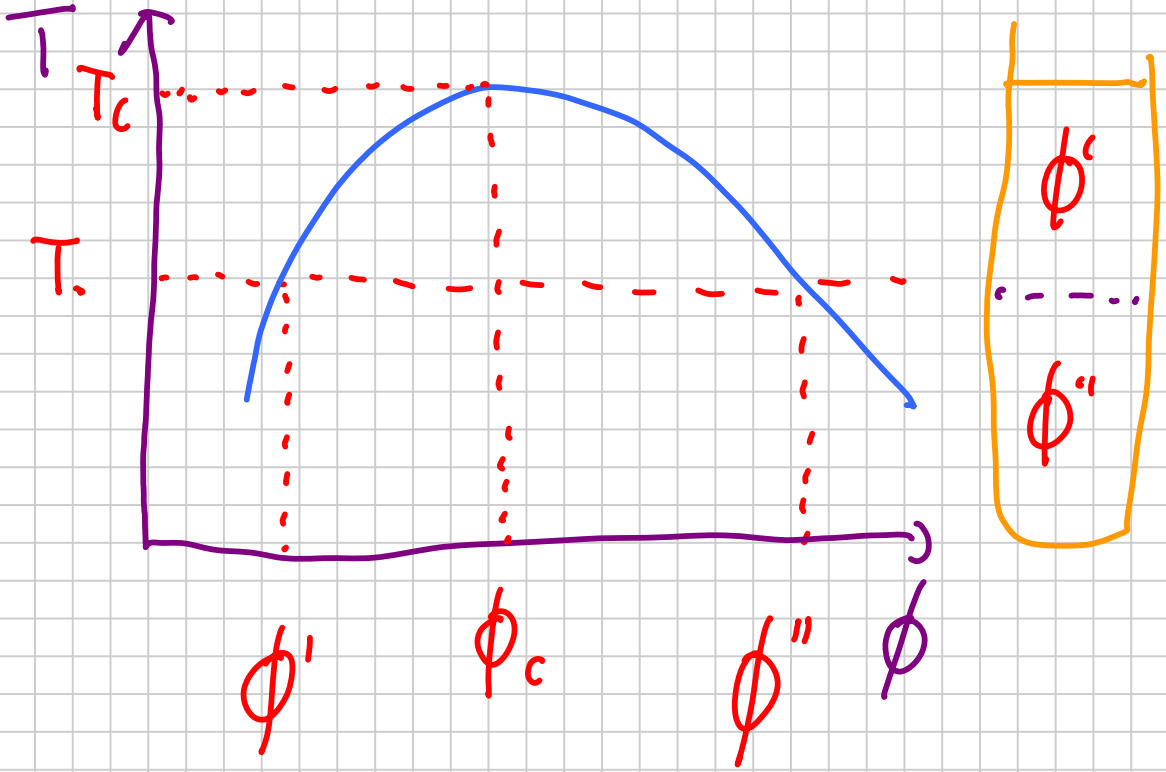
but: no intersection in

microscopic dimensions!

cf. theory of real gases

Important consequences:

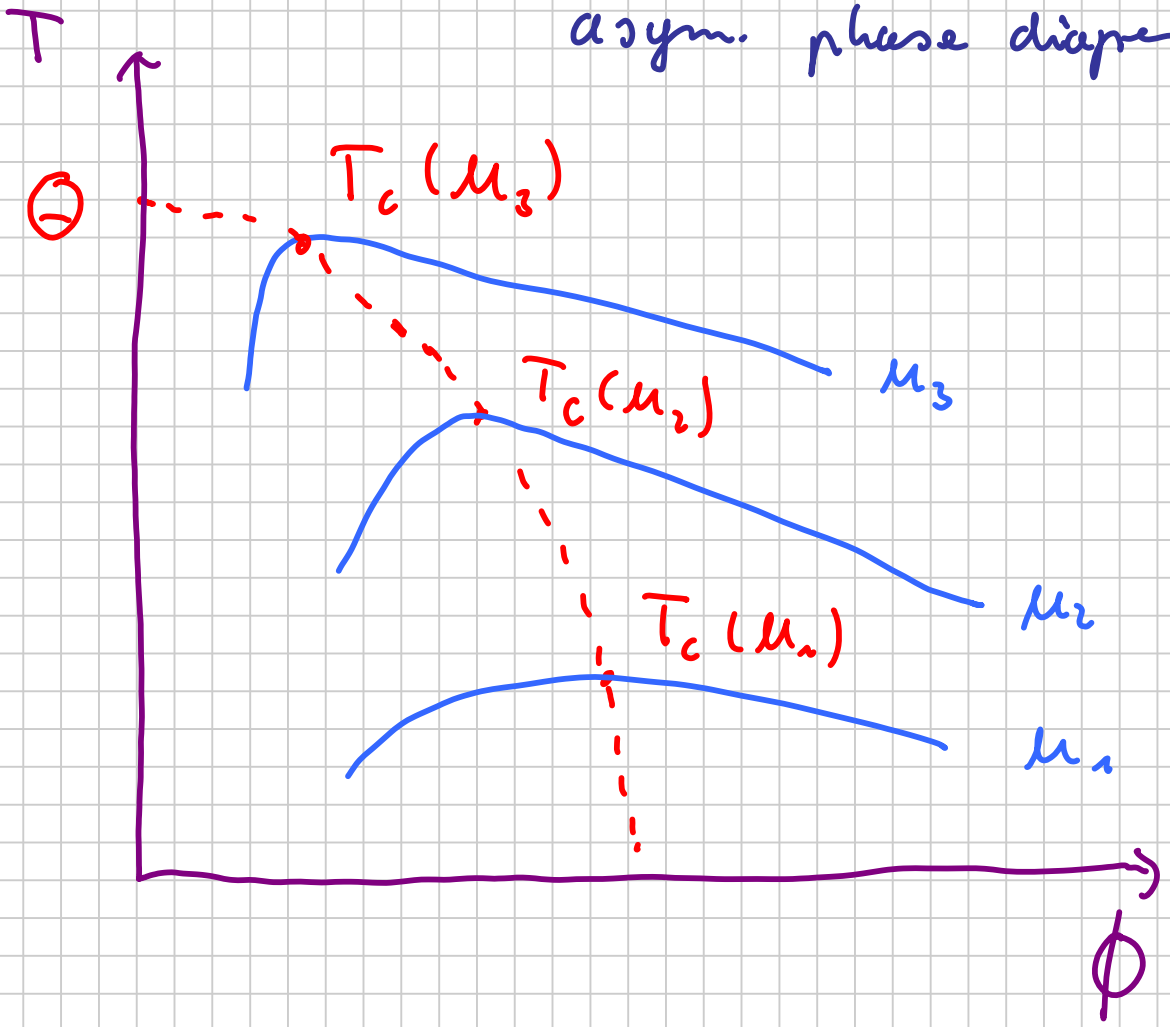
Demixing in concentrated solutions



Demixing leads to coexistence of two phases differing in volume fraction of polymer

Polymers $M_3 > M_2 > M_1$

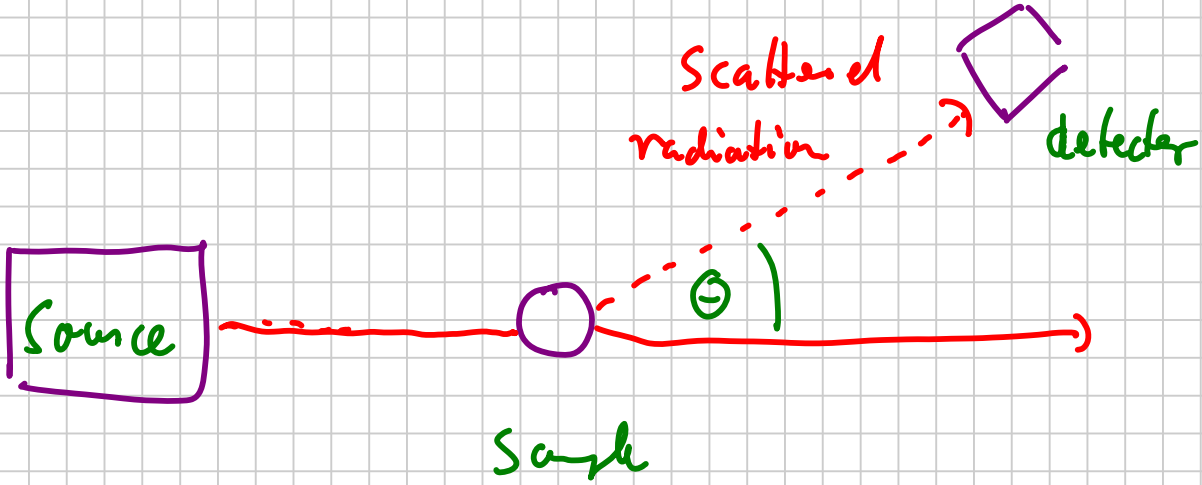
asym. phase diagram



Θ temperature = critical temperature for infinite molecular weight

Experimental approach

Scattering methods

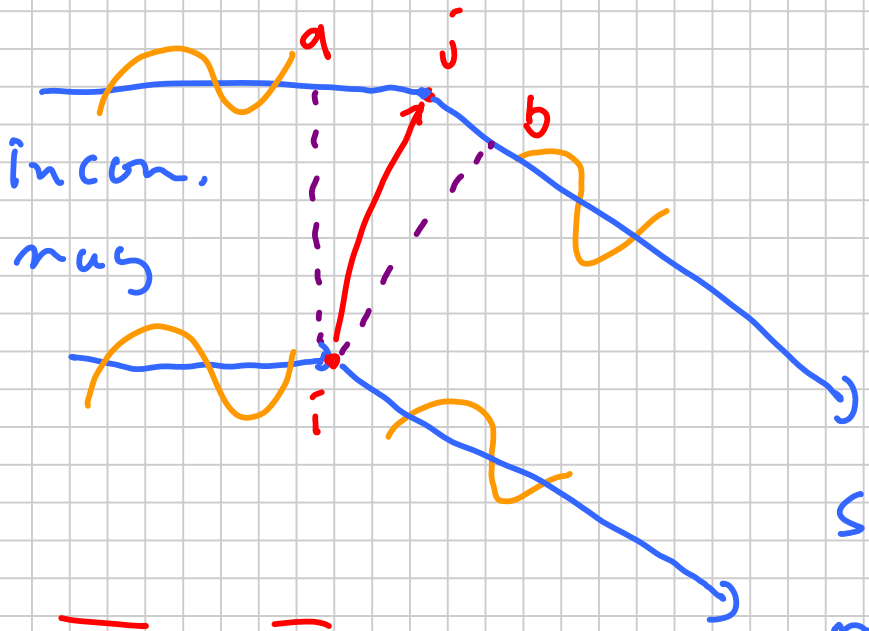


light (Laser)

X-rays (synchrotron)

neutrons

Dimensions of macromolecules can be determined through interference of scattered beams



$\overline{aj} + \overline{jb}$:

difference in path → interference

⇒ can be used to determine

radius of gyration $\langle s^2 \rangle$