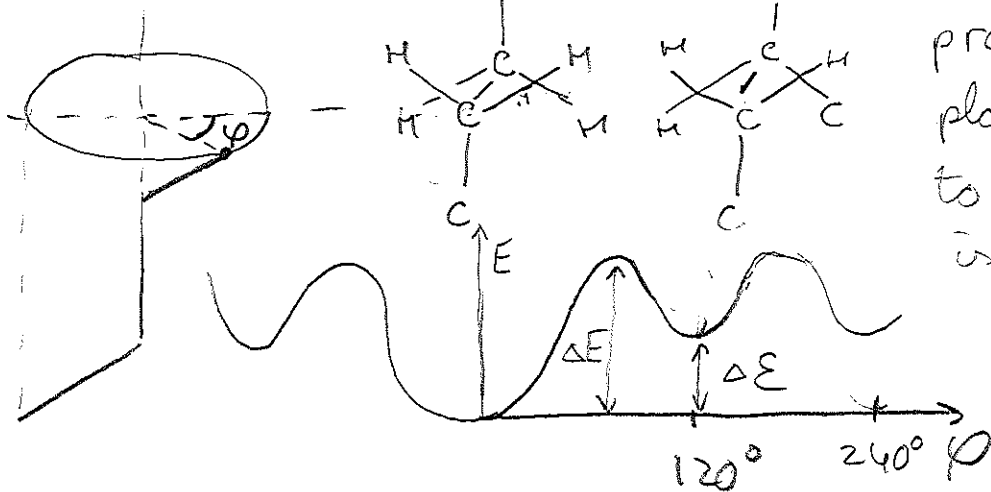


- $\text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \dots$ polyethylene = $(\text{CH}_2)_N$
 ↑
 monomer ; N - degree of polymerization $\sim 10^5$

Branching



Angle between the C-C bonds $\approx 109^\circ$



projected to the
 plane orthogonal
 to the C-C bond
 $\approx 120^\circ$

Probability to turn $\sim e^{-\frac{\Delta E}{T}}$

Persistence length $l_p = l_0 e^{\frac{\Delta E}{T}}$

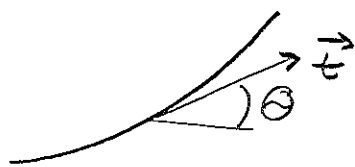
For $l < l_p$ - rigid chain

For $l > l_p$ - flexible chain

Persistence time $t = t_0 e^{\frac{\Delta E}{T}}$

Elastic description

$$H = \frac{c}{2} \int \left(\frac{d\theta}{dl} \right)^2 dl$$



Energy does not depend on angle but depends on the curvature

$$H = \frac{c}{2} \sum \kappa^2 \theta_k^2 \Rightarrow |\theta_k|^2 = \frac{2T}{c \kappa^2} \Rightarrow$$

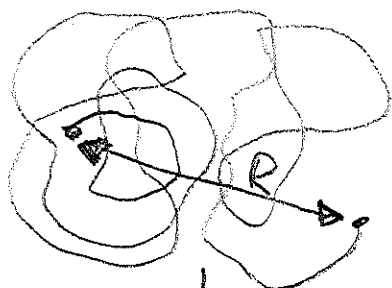
$$\langle (\theta(l) - \theta(0))^2 \rangle = \frac{4T}{c} \int \frac{1 - \cos \kappa l}{\kappa^2} (d\kappa) \approx \frac{2T}{c} l$$

$$\langle \cos(\theta(l) - \theta(0)) \rangle = e^{-\frac{\langle (\theta(l) - \theta(0))^2 \rangle}{2}} = \exp\left(-\frac{lT}{c}\right)$$

Chain is uncorrelated on large distances

Persistence length is $l_p = \frac{c}{T}$

How does the distance between the ends depend on l ?



$$R = \int_0^L \vec{t}(l) dl, \quad \langle R^2 \rangle = \int_0^L \int_0^L \langle \vec{t}(l_1) \cdot \vec{t}(l_2) \rangle dl_1 dl_2 =$$

$$= \int_0^L \int_0^L e^{-\frac{T}{c} |l_1 - l_2|} dl_1 dl_2 = 2 \left(\frac{c}{T} \right)^2 \left(\frac{LT}{c} - 1 + e^{-\frac{LT}{c}} \right)$$

for small L, T , $LT \ll c \Rightarrow \langle R^2 \rangle = L^2 \left(1 - \frac{LT}{3c} \right) \Rightarrow$

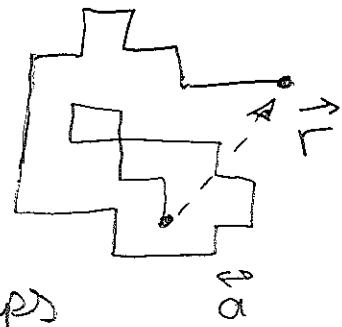
almost straight but deviation $\underline{u \sim L^{3/2}}$

for large L, T , $LT \gg c \Rightarrow \langle R^2 \rangle = \underline{\underline{\frac{2cL}{T}}}$

Ideal chain \Leftrightarrow simple random walk

Entropy $S_N(r) = \ln(\mathcal{N}_N(r))$,

where $\mathcal{N}_N(r)$ - number of different walks going from 0 to \vec{r} in N steps



$$\sum_r \mathcal{N}_N(r) = z^N \quad (z = \text{coordination number})$$

$$\vec{r} = \vec{a}_1 + \vec{a}_2 + \dots + \vec{a}_N$$

$$\langle r^2 \rangle = \sum_{nm} \langle a_n \cdot a_m \rangle = \sum_n \langle a_n^2 \rangle = N a^2 \equiv R_0^2$$

random walk has size $R_0 \sim N^{1/2} a$

Distribution function for r

$$P(r) = \frac{\mathcal{N}_N(r)}{\sum_r \mathcal{N}_N(r)} \text{ is Gaussian for large } N$$

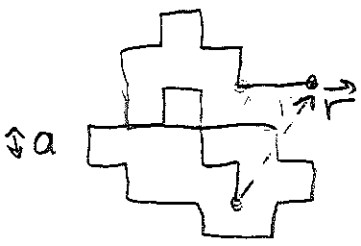
$$P(r) \approx \frac{1}{N^{d/2}} e^{-\frac{d}{2} \frac{r^2}{\langle r^2 \rangle}}$$

Thus entropy $S(r) = S(0) - \frac{3}{2} \frac{r^2}{R_0^2}$

and $F = E - TS = F(0) + \frac{3}{2} \frac{T r^2}{R_0^2} \leftarrow \text{elastic energy}$

Ideal chain \Leftrightarrow simple random walk

3a



Entropy $S_N(r) = \ln(N_N(r))$, where

$N_N(r)$ - number of different walks

going from 0 to \vec{r} in N steps

$$\sum_r N_N(r) = z^N \quad (z = \text{coordination number})$$

$$\vec{r} = \vec{a}_1 + \vec{a}_2 + \dots + \vec{a}_N$$

$$\langle r^2 \rangle = \sum_{nm} \langle a_n \cdot a_m \rangle = \sum_n \langle a_n^2 \rangle = Na^2 \equiv R_0^2$$

random walk has size $R_0 \sim N^{1/2}a$

Distribution function for r

$$p(r) = \frac{N_N(r)}{\sum_r N_N(r)} \quad \text{is Gaussian for large } N$$

$$\text{In 1D} \quad p(x) \approx N^{-1/2} \exp\left(-\frac{x^2}{2\langle x^2 \rangle}\right) =$$

Proof: Number of paths with N steps with displacement

M to the right means $\frac{N+M}{2}$ steps ^{to the} right and $\frac{N-M}{2}$ to the left

$$\text{This is } \frac{N!}{\left(\frac{N+M}{2}\right)! \left(\frac{N-M}{2}\right)!}$$

Normalising we obtain

(4)

$$P_N(M) = \frac{N!}{2^N \left(\frac{N+M}{2}\right)! \left(\frac{N-M}{2}\right)!}$$

Using $X! \approx \sqrt{2\pi X} X^X e^{-X} \Rightarrow$

$$P_N(M) \approx \frac{N^N e^{-N} \sqrt{N}}{\left(\frac{N+M}{2}\right)^{\frac{N+M}{2}} \left(\frac{N-M}{2}\right)^{\frac{N-M}{2}} e^{-N} \sqrt{N^2 - M^2}}$$

for $M \ll N$ we have

$$P_N(M) \sim \frac{1}{\sqrt{\pi} \left(\frac{1+M/N}{2}\right)^{\frac{N+M}{2}} \left(\frac{1-M/N}{2}\right)^{\frac{N-M}{2}}} = \frac{1}{\left(\frac{1-M/N}{2}\right)^{\frac{N}{2}} \left(\frac{1+M/N}{2}\right)^{\frac{N}{2}}} \frac{e^{-\frac{M^2}{2N}}}{\sqrt{\pi} e^{-\frac{M^2}{2N}} e^{\frac{M^2}{2N}}} \sim \frac{1}{\sqrt{\pi}} e^{-\frac{M^2}{2N}}$$

$$P_N(x) \approx \frac{1}{\sqrt{\pi}} e^{-\frac{x^2}{2\langle x^2 \rangle}}$$

for 3D $P_N(r) \approx \frac{1}{N^{3/2}} e^{-\frac{3r^2}{2\langle r^2 \rangle}} = \frac{1}{N^{3/2}} e^{-\frac{3}{2} \frac{r^2}{R_0^2}}$

Thus entropy $S(r) = S(0) - \frac{3}{2} \frac{r^2}{R_0^2}$

and $F = E - TS = F(0) + \frac{3}{2} \frac{T r^2}{R_0^2}$

elastic energy

If we pull the chain then

$$f = \frac{\partial F}{\partial r} \Rightarrow \langle r \rangle_f = f \frac{R_0^2}{3T}$$

holds if $\langle r \rangle \ll Na$

From dimensional estimates tension is the same along the chain \Rightarrow

$$\Rightarrow f \sim N; r = g(f, T, R_0 = N^{1/2} a) = R_0 \left(\frac{f R_0}{T}\right)^{1/2} \sim N^{1/2} \frac{f R_0}{T}$$

$$x=1 \Rightarrow r \sim \frac{f R_0^2}{T}$$

An Ideal chain in external potential $\mathcal{U}(r)$ (5)

Let us introduce

$$r^1 = r_1, \quad r = r_N$$

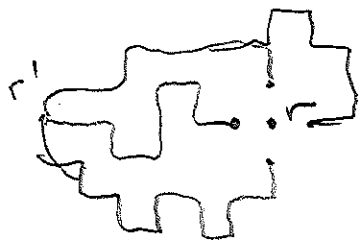
$$z^N G_N(r^1, r) = \sum_{\text{all paths}} \exp\left[-\frac{1}{T} \{ \mathcal{U}(r_1) + \mathcal{U}(r_2) + \dots + \mathcal{U}(r_N) \}\right]$$

z - coordination number of the lattice

$$G_N(r^1, r) = G_N(r, r^1) \quad ; \quad G_{N=0}(r^1, r) = \delta_{r^1, r}$$

for $N+1$ chain

$$G_{N+1}(r^1, r) = \frac{1}{z} \sum_{r''}^{\text{over all neighbours of } r} G_N(r^1, r'') \exp\left(-\frac{\mathcal{U}(r)}{T}\right)$$



Consider smooth potential and $\mathcal{U}(r) \ll T$ then

we can expand

0 after summing

$$G_{N+1}(r^1, r) = \frac{1}{z} \left(1 - \frac{\mathcal{U}(r)}{T}\right) \sum_{r''} G_N(r^1, r'') + (\vec{r} - \vec{r}'') \cdot \nabla_r G_N + \frac{1}{2} (\vec{r} - \vec{r}'')_a (\vec{r} - \vec{r}'')_B \nabla_a \nabla_B G + \dots \Rightarrow$$

$$G_{N+1} - G_N = -\frac{\mathcal{U}(r)}{T} G_N + \frac{a^2}{6} \nabla^2 G_N(r^1, r) \Rightarrow$$

$$-\frac{\partial G}{\partial N} = -\frac{a^2}{6} \nabla^2 G + \frac{\mathcal{U}(r)}{T} G$$

similar to the Schrödinger equation!

for $\mathcal{U}=0$ we just derived the Gaussian distribution of the number of paths

As in quantum mechanics we can expand in eigenfunctions

$$G_N(r', r) = a^3 \sum_k U_k^*(r') U_k(r) \exp(-N \epsilon_k)$$

where

$$\left(-\frac{a^2}{6} \nabla^2 + \frac{V(r)}{T} \right) U_k(r) = \epsilon_k U_k(r)$$

Thus we should find the "wave functions" $U_k(r)$

$$\rightarrow G_N(r', r)$$

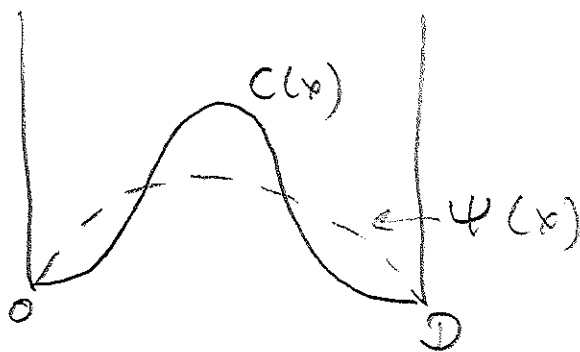
$$\text{Concentration } a^3 C(s) = \frac{\sum_{r', r} \sum_{N'=0}^N G_{N'}(r', s) G_{N-N'}(s, r)}{\sum_{r', r} G_N(r', r)}$$

Since $G_N \sim \exp(-N \epsilon_k)$ then usually lowest ϵ_0 is important \Rightarrow Ground state dominance

$$U_0(r) = \psi(r) \Rightarrow$$

$$C(r) = N |\psi^2(r)|$$

Chain between two repulsive walls



the same problem as a particle in potential well (7)

$$-\frac{a^2}{6} \nabla^2 u_k = \epsilon_k \Rightarrow u_0 = C \sin \frac{\pi x}{D}$$

$$\epsilon_0 = \frac{1}{6} \left(\frac{\pi a}{D} \right)^2$$

$$C \propto u^2 \sim \sin^2 \frac{\pi x}{D}$$

excited states $u_{n,g} \sim \sin \frac{\pi n x}{D} \exp(i(g_y y + g_z z))$

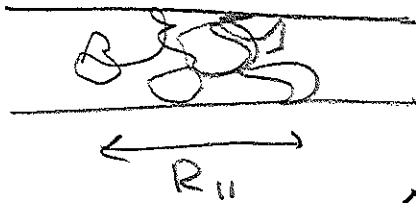
$$\epsilon_{n,g} = \frac{a^2}{6} \left[\left(\frac{\pi}{D} \right)^2 n^2 + g^2 \right]$$

the error due to higher states $\sim \exp(-N(\epsilon_1 - \epsilon_0)) \sim \exp(-\text{const} \frac{R_0^2}{D^2}) \Rightarrow$ accurate for $R_0 \gg D$

main term in the statistical weight $e^{-\epsilon_0 N} \Rightarrow$

$$\Delta S = -\frac{\pi^2}{6} \frac{R_0^2}{D^2} \Rightarrow \text{confinement energy } F = \frac{\pi^2}{6} \frac{R_0^2}{D^2} T$$

simple estimate



$R_{||} = R_0$ since walls do not

affect parallel motion

$$\Delta S \sim N \text{ and } \Delta S = f \left(\frac{R_0}{D} \right) \Rightarrow$$

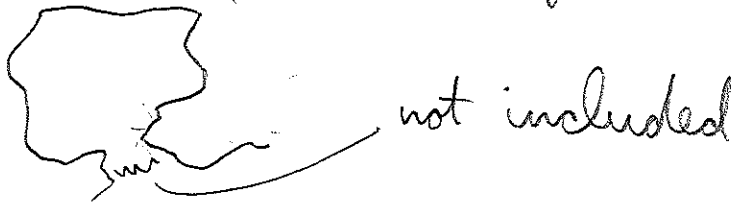
$$\Delta S \sim \frac{R_0^2}{D^2}$$

Problem: find concentration profile for the chains near attractive wall

Real chains

(8)

In ideal chain we took into account only interactions between neighbours along the chain



In reality polymers can not cross each other \Rightarrow

- Self-avoiding walks (forbidden crossing)

From the simulations

Total number of SAW of N steps for large N

$$\mathcal{N}_N(\text{tot}) \approx \sum_{\tilde{z}}^N N^{\gamma-1} \quad \text{for ideal } \approx z^N$$

$$\tilde{z} < z \quad (\text{for 3D cubic lattice } \tilde{z} = 4.68)$$

\tilde{z} is not universal - depends on lattice

- γ is universal (depends only on the dimensionality d)

for 3D lattice $\gamma_3 \equiv 7/6$

-4- 2D - " - $\gamma_2 \equiv 4/3$

1D $\mathcal{N}(N) = 2 \Rightarrow \tilde{z} = 1, \gamma_1 = 1$

Self avoiding is very important for small d
and not so important for large d

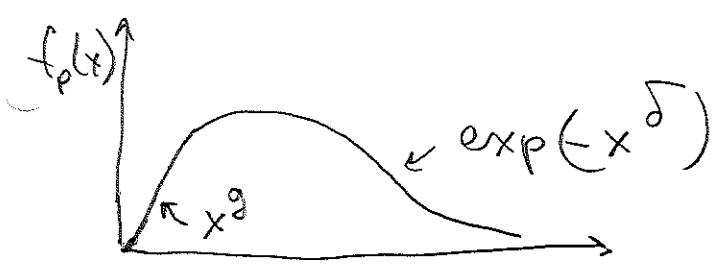
Average end to end distance (size)

$$\langle r^2 \rangle^{1/2} \equiv R_F \equiv a N^{\nu} \quad (\nu_3 \approx \frac{3}{5}, \nu_2 = \frac{3}{4}, \nu_1 = 1)$$

Distribution function depends on $\frac{r}{R_F}$

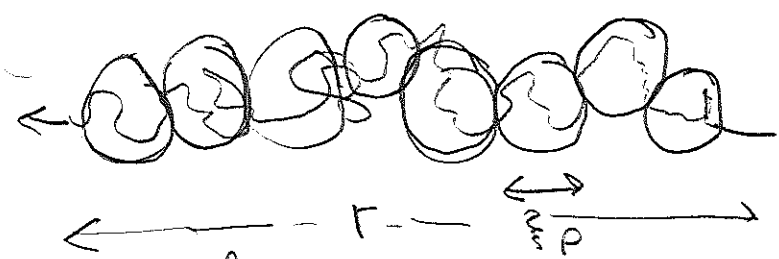
$$P_N(r) = \frac{1}{R_F^d} f_p\left(\frac{r}{R_F}\right) \quad (a \ll r \ll Na)$$

$$\int P_N(r) d^d r = \int f_p(x) d^d x = 1$$



We can relate δ to ν .

Consider real chain under action of large force such that $f R_F \gg T$. Then the chain breaks up into a series of "blobs" with size $\xi_p \sim \frac{T}{f}$



within each blob $(x \ll T) \Rightarrow$
 \Rightarrow force can be neglected \Rightarrow

\Rightarrow real chain. For $r > \xi_p$ - independent blobs,

Number of monomers per blob from the $\xi_p \approx a N_p \Rightarrow$
 $N_p \approx \left(\frac{T}{af}\right)^{1/\nu}$. Total number of blobs is $N/N_p \Rightarrow$

elongation $\langle r \rangle \approx \frac{N}{N_p} \xi_p \approx \frac{Na \left(\frac{fa}{T}\right)^{\frac{1}{\nu}-1}}{}$. But from

The distribution function $S \propto -\left(\frac{r}{R_F}\right)^\delta \Rightarrow F \sim T \left(\frac{r}{R_F}\right)^\delta - fr$

and minimizing obtain that $|\delta = \frac{1}{1-\nu}|$

Flory scaling

(P. Flory 1949)

10

Consider chain with radius R and number N

Internal monomer concentration is $C_{int} \equiv \frac{N}{R^d}$

There is repulsion energy due to the monomer-monomer interactions. It is \propto to the number of pairs $\sim c^2$ energy density

$$f_{rep} \approx T \nu(T) c^2 \quad (\nu \text{ has dimension of volume})$$

We replace $\langle c^2 \rangle \rightarrow \langle c \rangle^2 \sim C_{int}^2$ (mean field)

Then the total repulsive energy $F = \int f_{rep} dV$

$$F_{rep} \approx T \nu(T) C_{int}^2 R^d = TV \frac{N^2}{R^d}$$

favours increase of R

Let us add elastic energy due to entropy.

For an ideal chain $F_{el} \approx \frac{TR^2}{Na^2} \Rightarrow$

$$\frac{F}{T} \approx \nu \frac{N^2}{R^d} + \frac{R^2}{Na^2} \quad \text{minimising } F \Rightarrow$$

$$R_F^{d+2} \approx N^3 \nu a^2 \quad \text{and} \quad R_F \propto N^\nu$$

with

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

accurate $\sim 1\%$
(exact in $d=1, 2, 4$)

For $d = 4$ $\nu = \frac{1}{2} \Rightarrow$ ideal chain. Why? 11

Since R is not less than $R_{ideal} = N^{1/2} a$
then Repulsive energy

$$F_{rep} \geq \nu T \frac{N^2}{R_{id}^d} \approx T \frac{\nu}{a^d} N^{2-d/2}$$

Thermal energy $\sim T \Rightarrow$

$$\frac{F_{rep}}{F_{th}} \leq N^{2-d/2}$$

For $d > 4$ repulsion is not important \Rightarrow
chains are ideal for $d \geq 4$

Flory result \rightarrow cancellation of 2 errors

1. repulsive energy over estimated correlations
are ignored

2. elastic energy also over estimated since
it should be $T \frac{R^2}{R_F^2}$ rather than $T \frac{R^2}{R_0^2}$

But as a result \rightarrow very accurate formula

if we improve on 1 or 2 then it would
be worse.

Another derivation of the Flory scaling

Noninteracting chain $M_0 = \int \left(\frac{dr}{dt}\right)^2 dt$

Let us model interaction as $M_{in} \approx u a^d \sum_{i,j} \delta^{(d)}(r_i - r_j)$
then we obtain the Edwards hamiltonian

$$M = \int \left(\frac{dr}{dt}\right)^2 dt + u a^{d-4} \iint \delta^{(d)}(r(t_1) - r(t_2)) dt_1 dt_2$$

It is clear that u is irrelevant for $d > 4$

For $d < 4$ assuming similar scaling of two terms we obtain

$$\frac{r^2}{t} \sim \frac{t^2}{r^d} \Rightarrow r \sim t^{\frac{3}{d+2}} \Rightarrow$$

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