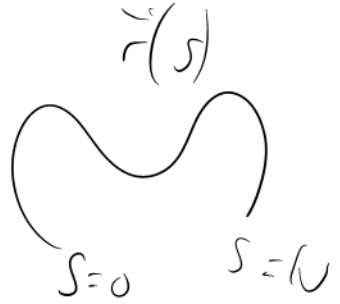
worm like chain $\quad s \in [0, N]$

$$\mathcal{H}_{tot} = \frac{\alpha}{2} \int_0^N ds \left(\frac{\partial \vec{u}}{\partial s} \right)^2$$



$\vec{u}$ tangent unit vector $\quad \vec{u} = \dfrac{\dfrac{\partial \vec{r}}{\partial s}}{\left| \dfrac{\partial \vec{r}}{\partial s} \right|}$

$$\mathcal{H}_{12} = \frac{\alpha}{2} \theta^2$$

constant bond length $b = |\Delta \vec{r}| \underset{\Delta s = 1}{=} \left| \dfrac{\Delta \vec{r}}{\Delta s} \right| = \left| \dfrac{\partial \vec{r}}{\partial s} \right|$

$$\Rightarrow \vec{u} = (1/b) \frac{\partial \vec{r}}{\partial s}$$

$$\frac{\partial \vec{u}}{\partial s} = \frac{1}{b} \frac{\partial^2 \vec{r}}{\partial s^2} = 1$$

2 addendi: elasticity, small scales

$$\mathcal{H}_{tot} = \frac{\alpha}{2b^2} \int_0^N ds \left(\frac{\partial^2 \vec{r}}{\partial s^2} \right)^2$$

§. Gaussian chain.

$$\mathcal{H}_{tot} = \frac{3 k_B T}{2 b^2} \int_0^N ds \left(\frac{\partial \vec{r}}{\partial s} \right)^2$$

1st derivative

entropy + connectivity

<u>large scales</u>

2. The Self-Avoiding Walk

2.1. Problem: excluded-volume interaction

(so far neglected)

- monomers repel each other (good solvent), cannot occupy the same space
- short-ranged in real space
- long-ranged along the backbone of the chain

→ This effect has the potential to fundamentally alter the chain conformations, such that it is no longer a Random Walk !

Rather : Self-Avoiding Walk (SAW)

Is it really important ?

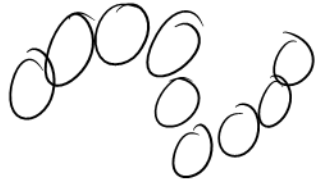
Let us try to estimate the effect via a simple Mean Field argument.

RW (≡ random walk) of N steps

in d-dimensional space, Bond length $L \simeq$

$\simeq$ monomer size $b \simeq$ range of interaction

(in real space)



Try to count the overlaps!

$$R \simeq b N^{1/2} \Rightarrow \text{density} \simeq \frac{N}{R^d} \simeq b^{-d} N^{1-d/2}$$

$\Rightarrow$ probability for a contact

(i.e. prob. that one part. monomer will see another monomer)

$$P \simeq \rho \underbrace{b^d}_{\text{volume of interaction range}} = N^{1-d/2}$$

total # of contacts: $pN = N^{2-d/2} =$

$= N^{1/2(4-d)} \equiv N^{\Sigma/2}$ with $\underline{\Sigma = 4-d}$

# of contacts is $\begin{cases} \text{giant} & d < 4 \\ \text{tiny} & d > 4 \end{cases}$

$\underline{\underline{d = 4}}$ is "upper critical dimension"

excluded volume interaction is $\begin{cases} \text{important} \\ \text{"relevant"} \end{cases} \quad d < 4$

$\begin{cases} \text{unimportant} \\ \text{"irrelevant"} \end{cases} \quad d > 4$

For chains in high spatial dimensions, R_N

is unchanged. But not in $d=3$, $d=2$, $d=1$

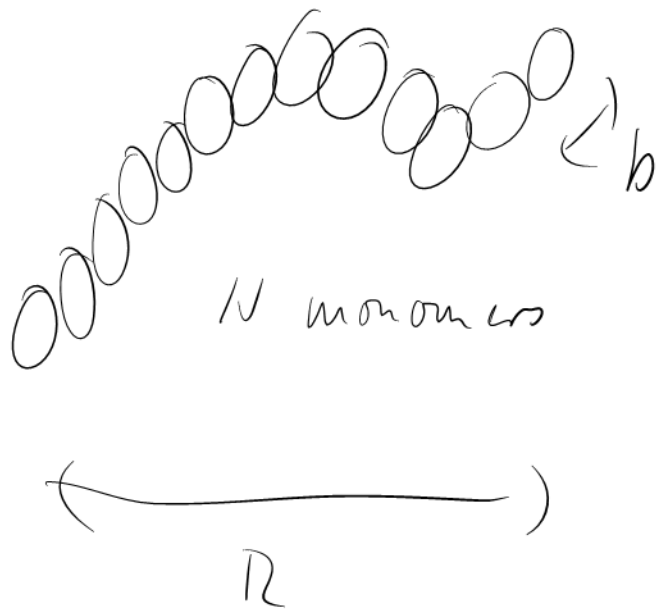
we live in $d=3$ → need to worry!

expect: SWELLING compared to RW

actually: $R \sim b N^{\nu}$ $\nu > 1/2$

WHY should this be a power law?

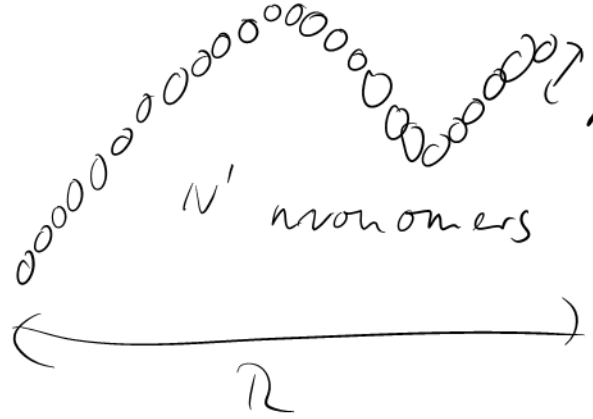
2.2. Scale Invariance



1st parameterization

$$R = R(N, b)$$

idea: Physics should not depend on the precise definition of what a monomer is!



2nd parameterization

$$R = R(N', b')$$

lumping groups of monomers into

"super-monomers" → "course-graining",

"renormalization group transformation"

$$N \longrightarrow N' = \lambda N \longrightarrow N'' = \mu N' = \lambda\mu N$$

$$N \longrightarrow\!\!\!\!\longrightarrow N'' = (\lambda\mu) N$$

$$b \longrightarrow b' = \phi(\lambda, b)\, b \longrightarrow b'' = \phi(\mu, b')\, b' =$$

$$= \phi(\mu, b')\, \phi(\lambda, b)\, b$$

Claim $\phi(\lambda, b) = \phi(\lambda)$ no dependence on b

Why? ϕ is a rescaling factor

→ " " dimensionless (just a number)

b is a length (meters)

→ There is a need to divide b by some other length, in order to get something dimensionless

→ BUT such a length does not exist!!!

absence of such a length means that

we assume scale invariance

Hence $\phi = \phi(\lambda)$

$$b \to b' = \phi(\lambda)\, b \longrightarrow b'' = \phi(\mu)\, b'$$

$$= \phi(\mu)\, \phi(\lambda)\, b$$

$$b \longrightarrow b'' = \phi(\lambda\mu)\, b$$

$$\boxed{\phi(\lambda\mu) = \phi(\lambda)\, \phi(\mu)}$$

$$\phi(\lambda\mu) = \phi(\lambda)\,\phi(\mu) \qquad \Big| \frac{d}{d\mu}$$

ϕ' ≡ derivative wrt argument

$$\lambda\,\phi'(\lambda\mu) = \phi(\lambda)\,\phi'(\mu) \qquad \Big| \mu = 1, \quad \underline{\underline{\phi'(1) = -\nu}}$$

$$\lambda\,\phi'(\lambda) = \phi(\lambda)(-\nu)$$

$$\frac{\phi'(\lambda)}{\phi(\lambda)} = \frac{1}{\lambda}(-\nu)$$

$$\frac{d}{d\lambda} \ln \phi(\lambda) = (-\nu)\frac{d}{d\lambda} \ln \lambda = \frac{d}{d\lambda}(-\nu) \ln \lambda = \frac{d}{d\lambda} \ln \lambda^{-\nu}$$

$$\ln \phi(\lambda) = \ln \lambda^{-\nu} + \underbrace{\text{const.}}_{=0}$$

$\lambda = 1 \Rightarrow \phi = 1$

$$\boxed{\phi(\lambda) = \lambda^{-\nu}}$$

power law

$$R(N, b) = R(N', b') = R(\lambda N, \lambda^{-\nu} b)$$

special value: $\lambda = N^{-1}$

$$R(N, b) = R(1, N^{+\nu} b)$$

$$R(N, b) = f(bN^{\nu})$$

special: $N = 1$, $R = b$, $f = b$

$b: \quad f(b) \qquad f(x) = x$

$$R = b N^{\nu}$$ power law !!

RW is just a special case $\nu = \frac{1}{2}$

For SAW, we expect $\nu \geq 1/2$ for $d < 4$

while $\nu = 1/2$ for $d \geq 4$

$\nu = ???$

2.3. Flory Theory

Mean Field argument as before → count # of contacts, but for SAW

$$R \simeq b N^{\nu} \Rightarrow \rho \simeq \frac{N}{b^d N^{\nu d}} = b^{-d} N^{1-d\nu}$$

$$\rho = b^d \rho = N^{1-d\nu}$$

contacts ~ $N^{2-d\nu}$

swelling → free energy penalty by entropic elasticity

$$\frac{1}{k_B T} F_{elastic} \propto \frac{R^2}{b^2 N} \sim \frac{b^2 N^{2\nu}}{b^2 N} = N^{2\nu - 1}$$

$$F_{total} \sim A N^{2 - d\nu} + B N^{2\nu - 1}$$

A, B independent of N

Balance requires that exponents are identical

$$2 - d\nu = 2\nu - 1$$

$$3 = (2+d)\nu$$

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

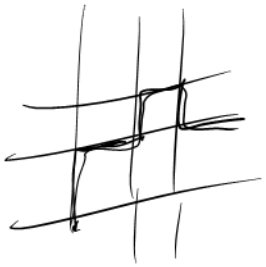
Flory prediction for ν

$$\nu = \nu_F$$

d	ν_F	exact
1	1	1
2	0.75	0.75
3	0.6	≈ 0.588
4	0.5	0.5

(conformal invariance)

2.4. Compute Simulations



(i) exact enumerations

up to N a few ten

(ii) Monte Carlo (MC) I : simple sampling

generate a RW chain, check for overlap

if yes, throw the whole chain away, start

from scratch, sample only the

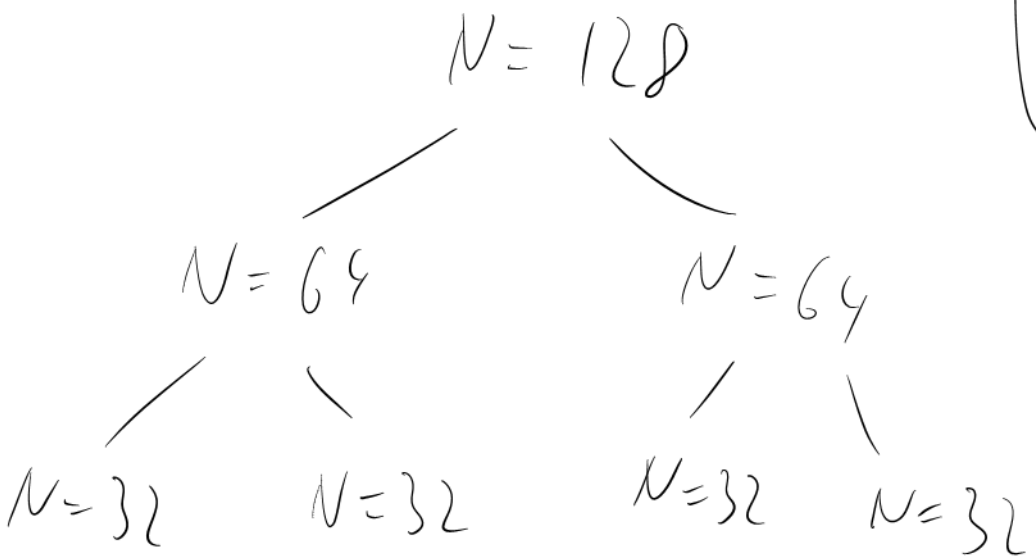
Successful chains

prob. survival ~ $\exp(-\alpha N)$ "attrition"

(iii) Rosenbluth sampling, "biased sampling"

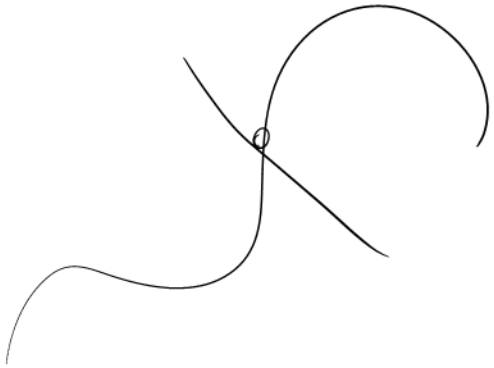
- self-crossing, try again, but punish this by a weighting factor < 1
- long chains: - many chains with a very small weight
  - few chains with weight of order one

(iv) MC: Dimerization



OUP, book edited by K. Binder, 1995
article by A. Sokal

(v) MC : Pivot : dynamic



fastest
known
algorithm

- pick one monomer randomly
- pick an axis randomly
- pick one end randomly
- rotate that by random angle
- check for overlap
- if yes, try again

Li, Madras, Sokal). Stat. Phys.

80, 661 (1995) $N \leq 0.8 \cdot 10^5$

$\nu = 0.5877 \pm 0.0006$

$$\frac{\langle R_e^2 \rangle}{\langle R_G^2 \rangle} = 6.254 \quad \underline{\text{not}} \quad \frac{R_G}{R_H}$$

B. D., Dirk Ritl, M. Steinlein, H. Krenn

JCP 117, 914 (2002)

$$\frac{R_G}{R_H} = 1.591 \pm 0.007$$

$N \leq 30\,000$

N. Clisby

PRL 104, 055702 (2010)

$N \leq 0.33 \cdot 10^8$

$\nu = 0.587597(7)$

$$\frac{\langle R_e^2 \rangle}{\langle R_h^2 \rangle} \simeq 6.2537$$

not $\frac{R_g}{R_H}$