Polymers

$$- CH_2 - CH_2 - CH_2 - \cdots$$ polyethylene

$$- CH_2 - CH - CH_2 - CH - \cdots$$ polystyrene

(benzene rings attached to the CH groups)

$$- CH_2 - CH - CH_2 - CH - \cdots$$
$$\qquad\quad | \qquad\qquad\quad |$$
$$\qquad\quad Cl \qquad\qquad\quad Cl$$
PVC polyvinyl chloride

Polymerisation : e.g. ethylene $H_2C = CH_2$

$$CH_2 = CH_2 + CH_2 = CH_2 \longrightarrow CH_3 - CH_2 - CH = CH_2$$
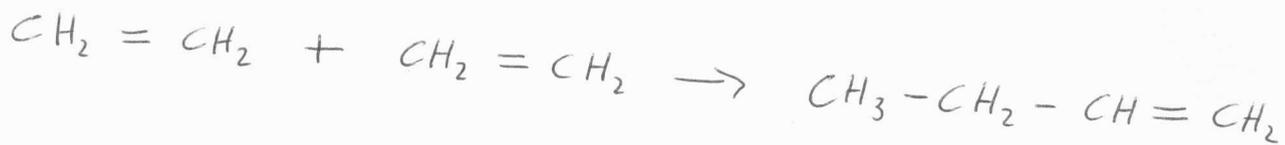
Polycondensation : e.g. polyesters, polypeptides

$$R_1 - C \underset{\diagdown OH}{\overset{\diagup O}{}} + OH - R_2 \longrightarrow R_1 - \overset{O}{\overset{||}{C}} - O - R_2$$

$$+ H_2O$$
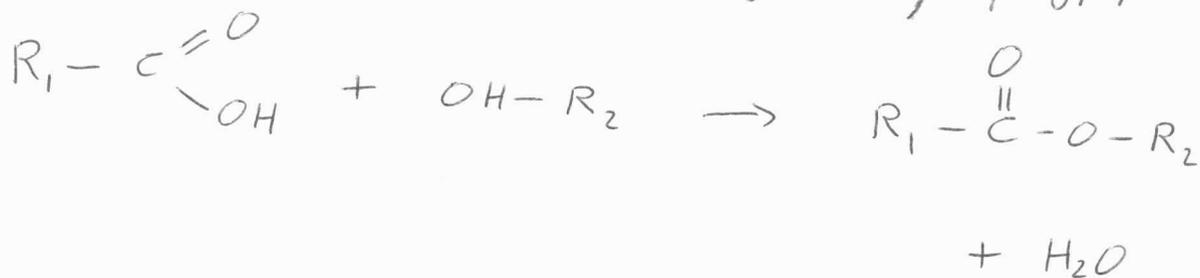
Polymer Physics

Polymers are flexible!   E.g. polyethylene $-CH_2-CH_2-\cdots$
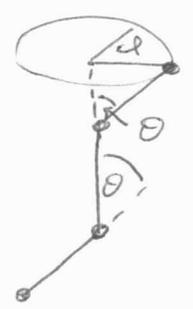
θ is fixed (given by the orbital structure of C)

φ can vary (for a single bond).

This is <u>one</u> mechanism for flexibility.

In gen. not all values of φ are equally likely:
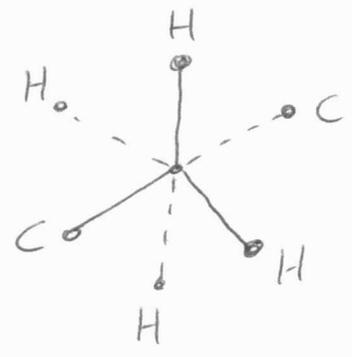
looking down along the C—C bond, this is one of the 3 low energy configurations
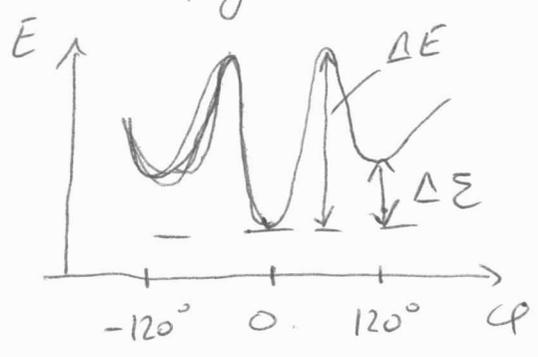
typical energy landscape

Two important energy scales: $\Delta \varepsilon \rightarrow$ fraction of links which are noted with respect to the minimum energy config. ($\varphi = 0$)

$\Delta E \longrightarrow$ time it takes to switch conformations

$$\frac{N(\varphi=120)}{N(\varphi=0)} = e^{-\Delta\varepsilon/T}$$

$$\Rightarrow \quad \ell_p \sim \ell_o \, e^{\Delta\varepsilon/T} \quad \text{in this model}$$

$\Delta\varepsilon/T \lesssim 1 \quad \rightarrow$ very flexible polymer

(short persistence length: $\ell_p \sim \ell_o$)

if $\Delta\varepsilon/T > 1$ but not too large, the polymer is still flexible at large enough length scales

(i.e. at length scales $\gg \ell_p$)

$\longrightarrow$ a generic conformation is not a straight molecule, but a coil:

10 - 100 nm typically
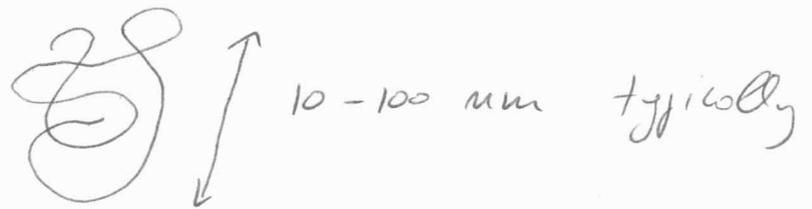
More precise (operational) definition of the persistence length:

$\vec{m}$ unit vector tangent to the curve
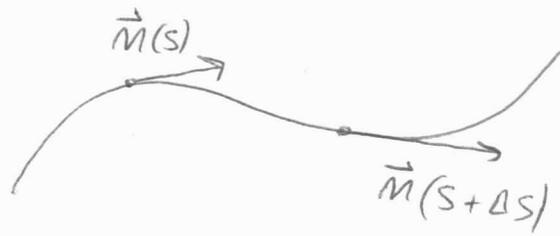
$$C(s) = \langle \vec{m}(s) \cdot \vec{m}(s+\Delta s) \rangle \propto e^{-\Delta s/\ell_p}$$

[one can check that $C(s)$ decays exponentially in any reasonable model]

Size of the ideal coil in terms of ℓ_p :
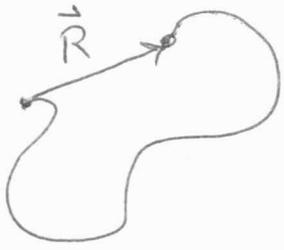
$$\int_0^L \vec{u}(s)\, ds = \vec{R} \qquad (EED)$$

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

$$\langle |\vec{R}|^2 \rangle = \left\langle \int_0^L ds\, \vec{u}(s) \cdot \int_0^L dt\, \vec{u}(t) \right\rangle = \int_0^L ds \int_0^L dt\, \langle \vec{u}(s) \cdot \vec{u}(t) \rangle$$

$$\langle \vec{u}(s) \cdot \vec{u}(t) \rangle = e^{-|s-t|/\ell_p}$$

take care of $s \gtrless t$:

$$\rightarrow \int_0^L ds \left\{ \int_0^s dt\, e^{-(s-t)/\ell_p} + \int_s^L dt\, e^{(s-t)/\ell_p} \right\}$$

$s-t = r$, $dt = -dr$

$s-t = -r$

$$\rightarrow \int_0^s dr\, e^{-r/\ell_p}$$

$$\rightarrow \int_0^{L-s} dr\, e^{-r/\ell_p}$$

$$\rightarrow \int ds \int dr = -\ell_p\left[(\ell_p e^{-L/\ell_p} - 1) - L\right]$$

$$\rightarrow \int ds \int dr = -\ell_p\left[\underbrace{(e^{-L/\ell_p} \quad \ell_p(e^{L/\ell_p} - 1) - L)} \right]$$

adding up :

$$\langle |\vec{R}|^2 \rangle = \ell_p \left\{ L - \ell_p e^{-L/\ell_p} + 1 + L - \ell_p + \ell_p e^{-L/\ell_p} \right\}$$

$$= \ell_p \left\{ 2L + 1 - \ell_p \right\} \simeq 2L\ell_p \quad \text{for } L \gg \ell_p .$$

So with $l_K = 2 l_p$ (Kuhn length)

and $\dfrac{L}{l_K} = N$ (number of Kuhn lengths in the chain)

$\Rightarrow \langle R^2 \rangle = l_K^2 N$ (ideal chain)

In summary: Kuhn length $l_K = 2 l_p$

and $\langle \vec{u}(s) \cdot \vec{u}(s + \Delta s) \rangle = e^{-\Delta s / l_p}$

Discrete : steps e.g. on a square lattice $\{ \vec{r_i} \}$

$$| \vec{r_i} | = l \quad \forall i$$

$$\langle R^2 \rangle = \left\langle \left(\sum_{i=1}^{N} \vec{r_i} \right)^2 \right\rangle = \sum_{i,j} \langle \vec{r_i} \cdot \vec{r_j} \rangle$$

$$\langle \vec{r_i} \cdot \vec{r_j} \rangle = l^2 \delta_{ij} \qquad \Rightarrow \langle R^2 \rangle = N l^2$$

So $l = l_K$ i.e. the step size of the discrete random walk corresponds to the Kuhn length.

|	polystyrene	ss DNA	ds DNA	actin filament
Examples : l_p	1.5 nm	1 nm	50 nm	20 μm

— Albert's meas. of persistence length of actin filaments —

Looking also at P3 :   lesson :

if correlations along the chain are _short_ range

(e.g. decay exponentially) then they do not

matter :   if you look at long enough scales

you get back the ideal nonatom walk, with

renormalized step size (the Kuhn length) .

Electron micrograph of part of
a muscle cell

sarcomere

myosin actin

(A)

Z disc   dark band   light band

myofibril   myofibril

(B)   sarcomere ~2.2 μm

light band   dark band   light band

Z disc   M line   Z disc

thick filament (myosin) ————
thin filament (actin) ————

(C)

2 μm

sarcomere

myosin thick filaments reverse polarity
at midline of sarcomere (the M line)

plus end of actin filaments
end on Z disc

minus end of actin filaments

Z disc
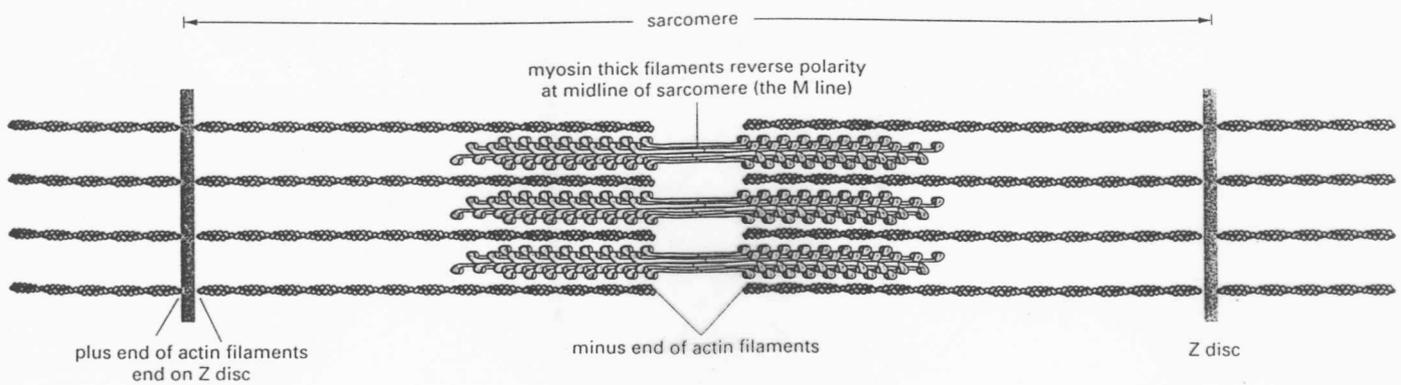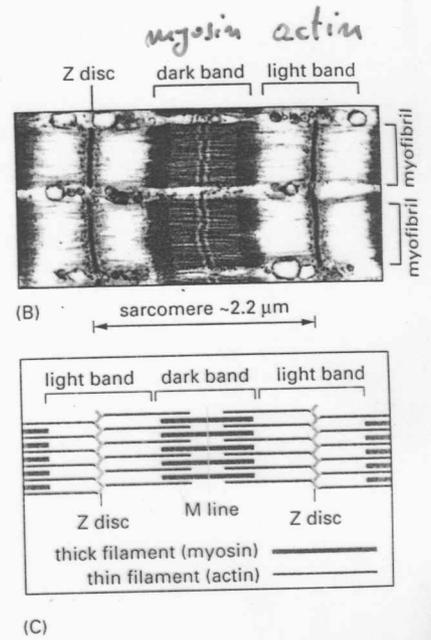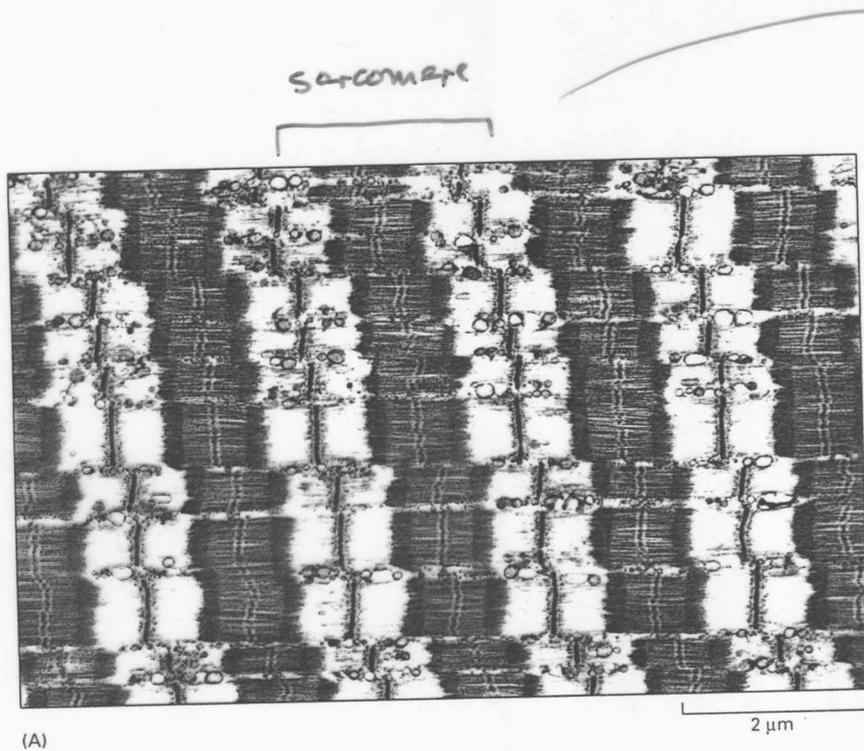
Actin : a 375 residues globular protein

minus end

ATP

HOOC

NH₂

plus end

(A)   (B)   (C)   (D)

minus end

plus end

ATP
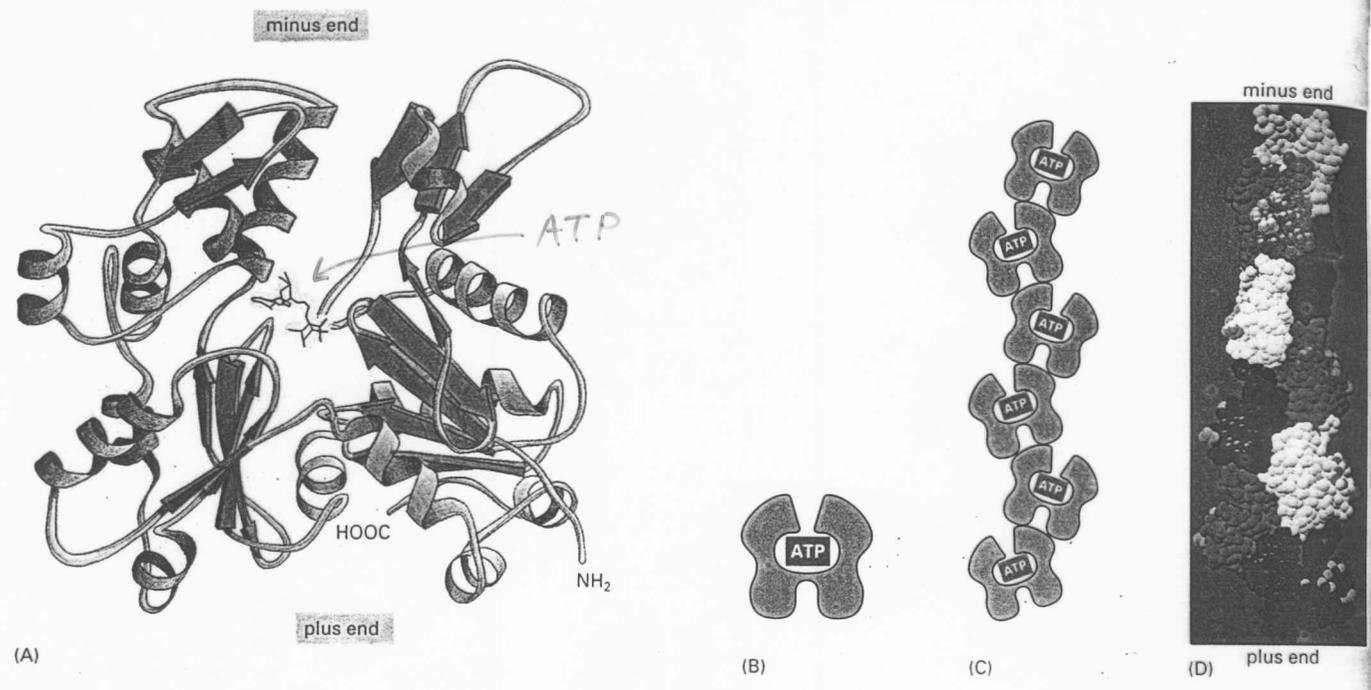
- Actin polymerizes in a two-stranded helix
  (8 mm diameter, 40 mm repeat distance)

- these polymers can be many μm long

- actin is one of the components of the muscle
   contraction system

Measurement of the persistence length of polymerized actin

[Phys. Rev. E 48 , 1642 (1993)]

$\vec{m}(s)$

$\vec{m}(s+\Delta s)$
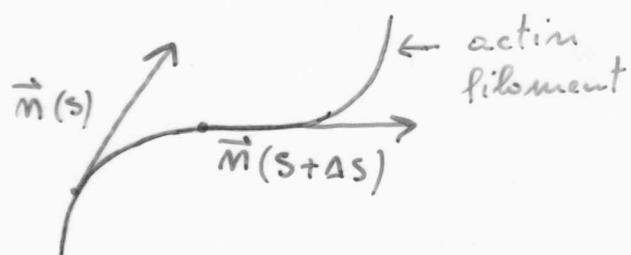
← actin filament

$$\langle \vec{m}(s) \cdot \vec{m}(s+\Delta s) \rangle \propto e^{-\Delta s/l_p}$$

l_p persistence length
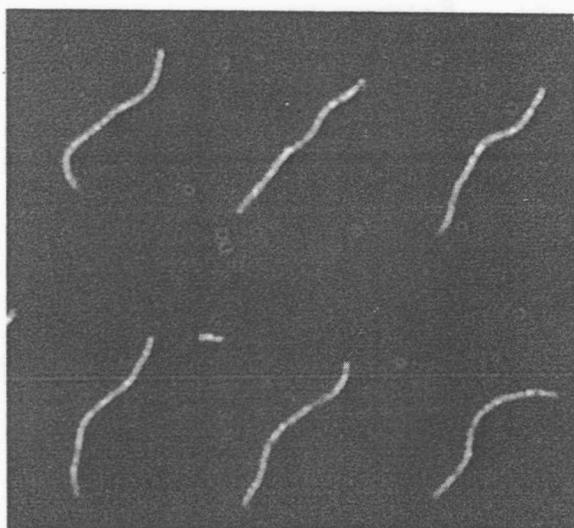
FIG. 2. An actin filament as observed by video fluorescence microscopy at time intervals of 10 s. (Successive images from left to right then top to bottom.)


distance x (μm)
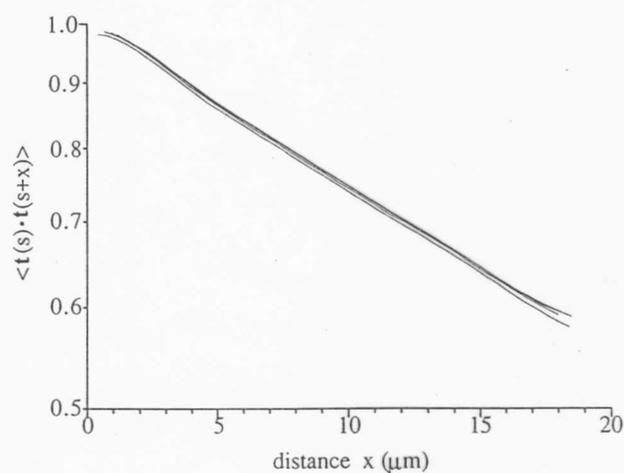
FIG. 6. Cosine correlation function (CCF) on a semilog plot for different values of the reparametrization parameter r_p shown in Fig. 5. The curves correspond to values of r_p of three, five, seven, and nine pixels (from top to bottom).

Result : $l_p = 17\ \mu m$

Entropic elasticity (ideal chain):

$$P(\vec{R}) \propto e^{-\frac{3R^2}{2\langle R^2 \rangle}} \qquad \text{(central limit theorem)}$$

factor of 3 :
$$P(x) \propto e^{-\frac{x^2}{2\langle x^2 \rangle}} \qquad \text{in 1-D}$$

$$\Rightarrow \quad p(x,y,z) \propto e^{-\frac{x^2}{2\langle x^2 \rangle}} \; e^{-\frac{y^2}{2\langle y^2 \rangle}} \; e^{-\frac{z^2}{2\langle z^2 \rangle}}$$

$$\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle = \ell_K^2 \frac{N}{3}$$

(because there are on average only $\frac{N}{3}$ steps along x etc.

or use the result $\langle R^2 \rangle = \ell_K^2 N$, $\langle x^2 \rangle = \frac{1}{3} \langle R^2 \rangle$)

number of states for the config. $\vec{R}$: $P(\vec{R}) \propto \Gamma(\vec{R})$

so $S/k = \ln \Gamma = \ln P(\vec{R}) + \text{const.}$ (all states equiprobable)
(some energy, assume)

$$\Rightarrow \quad S(\vec{R}) = -\frac{3R^2}{2N\ell_K^2} + \text{const.}$$

$$F = E - TS \; ; \quad \text{~~~~} \overset{\text{say}}{\text{even}} \text{ if } E \text{ is indep. of } \vec{R} :$$

$$F(\vec{R}) = T \frac{3R^2}{2N\ell_K^2} \quad \Rightarrow \quad \text{force} = -\frac{\partial F}{\partial R} = -\frac{3T}{N\ell_K^2} R$$

"spring constant" $\kappa = \dfrac{3kT}{N\ell_K^2}$

Notice the effect of temp. on the spring stiffness! $\longrightarrow$

Valid for $R \ll L$ (otherwise statistics is not Gaussian)
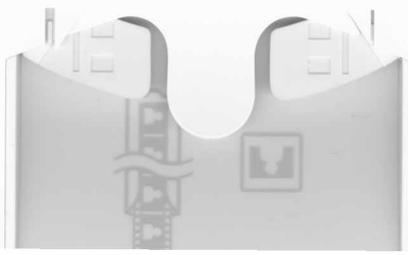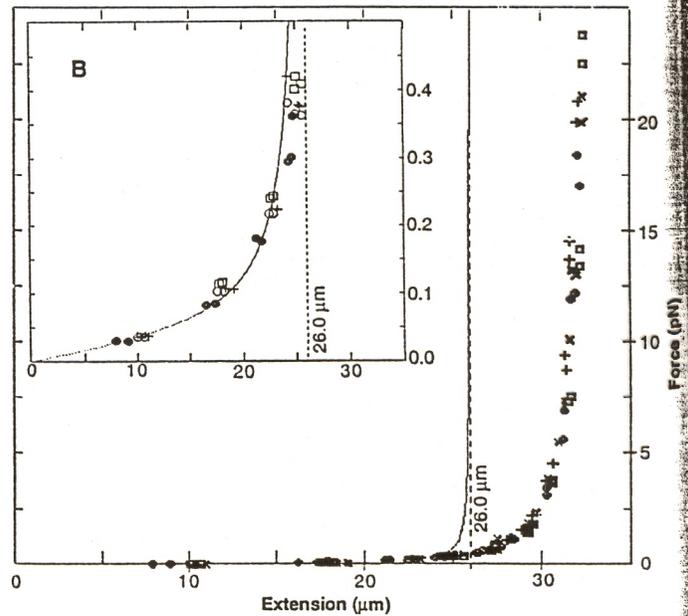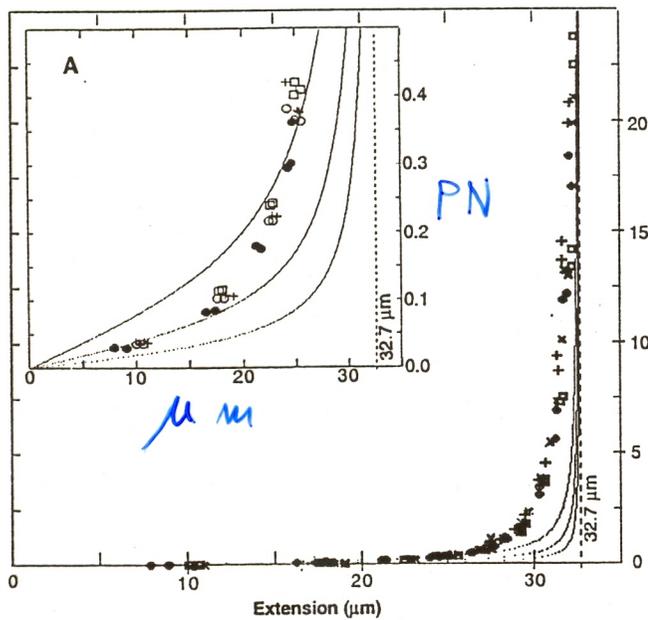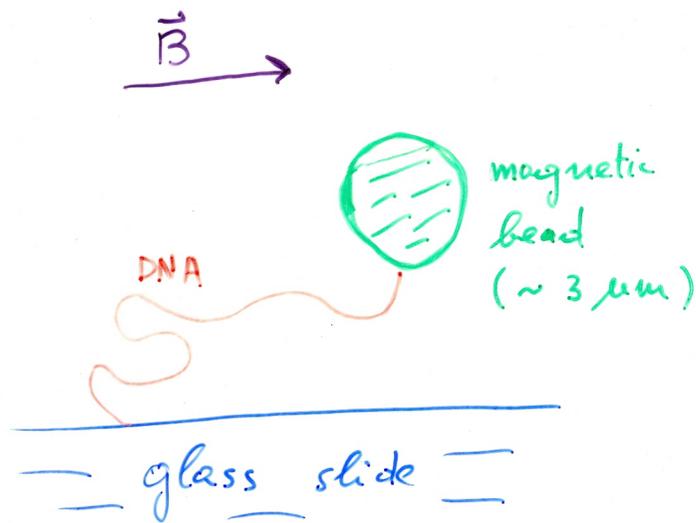
Fig. 3. (A) Force versus extension data for four different λ-dimer molecules (●, □, +, and ○) in 5 mM Na₂HPO₄ buffer (10 mM Na⁺, pH 8.3). Inset: expanded vertical scale (0 to 0.5 pN). Continuous curves are from Eq. 2 assuming L = 32.7 μm and b = 500 Å (top), 1000 Å (middle), and 2000 Å (lower). L = 32.7 μm was chosen to agree with the accepted value of 3.37 Å rise per base pair (30), not to fit the data. (B) The same data compared with a Langevin curve L = 26 μm and b = 1400 Å. These values were chosen to match the low-force slope.

Evanescent wave technique measures displacements with sub-nanometer resolution

scattered light

water

10 μm sphere

evanescent wave

$E \propto e^{-z/2\delta}$

z

glass

θ

incident beam
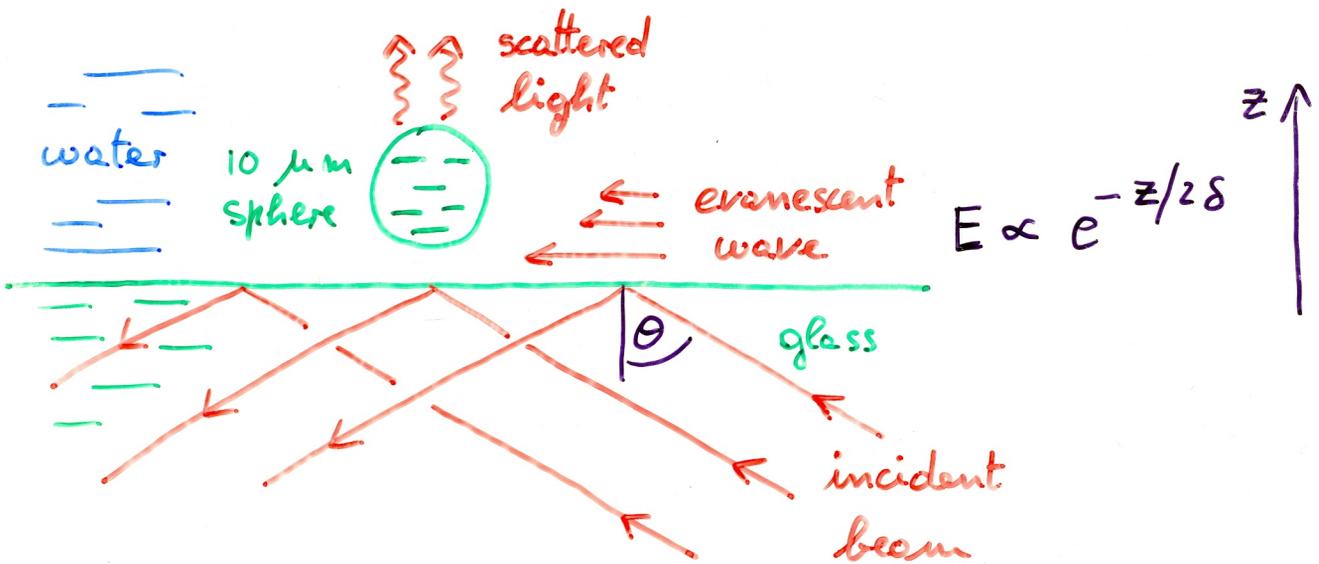
scattered intensity $I \propto e^{-z/\delta}$

$$\delta = \frac{\lambda}{4\pi \left(m_1^2 \sin^2\theta - m_2^2 \right)}$$

δ

θ_c $\pi/2$ θ
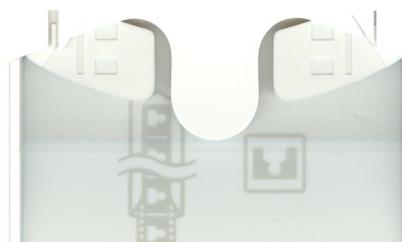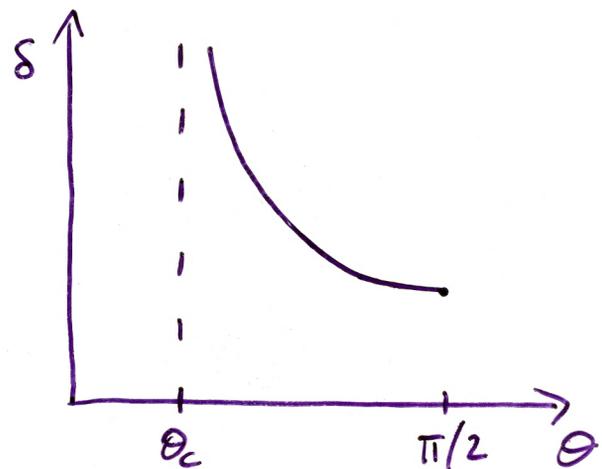
Measuring interaction potentials

Time series of the vertical position of the sphere $h(t)$

$\longrightarrow$ probability distribution $P(h)$

$$P(h) \propto e^{-\phi(h)/kT}$$

$\longrightarrow$ interaction potential $\phi(h)$

$h(t)$ $\qquad$ $P(h)$ $\qquad$ $\phi(h)$

$\rightarrow$ $\qquad$ $\rightarrow$

Tethered sphere :
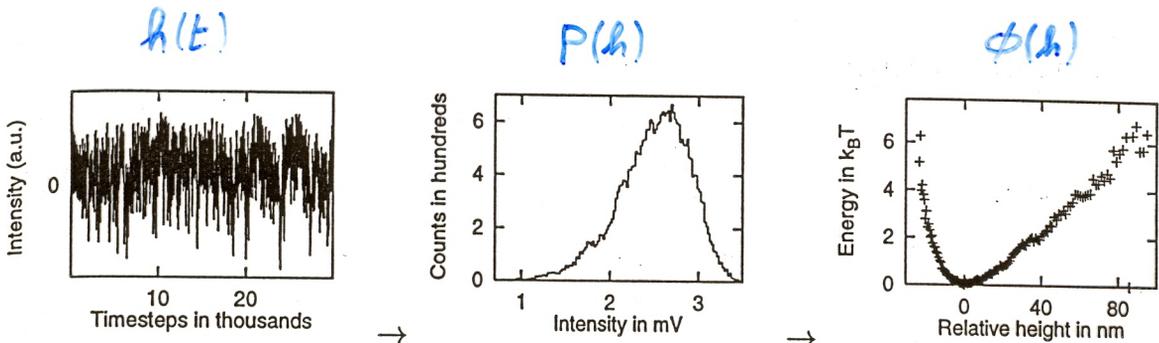
~ 50 nm $\qquad$ polystyrene coil
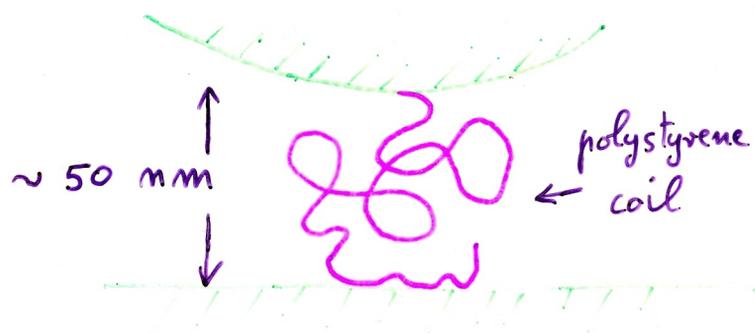
10 μm polystyrene sphere on glass surface

free
tethered

Intensity in a.u.

Time in seconds

Energy in $k_B T$

tethered

free

subtracting the
DLVO potential

Height in nm
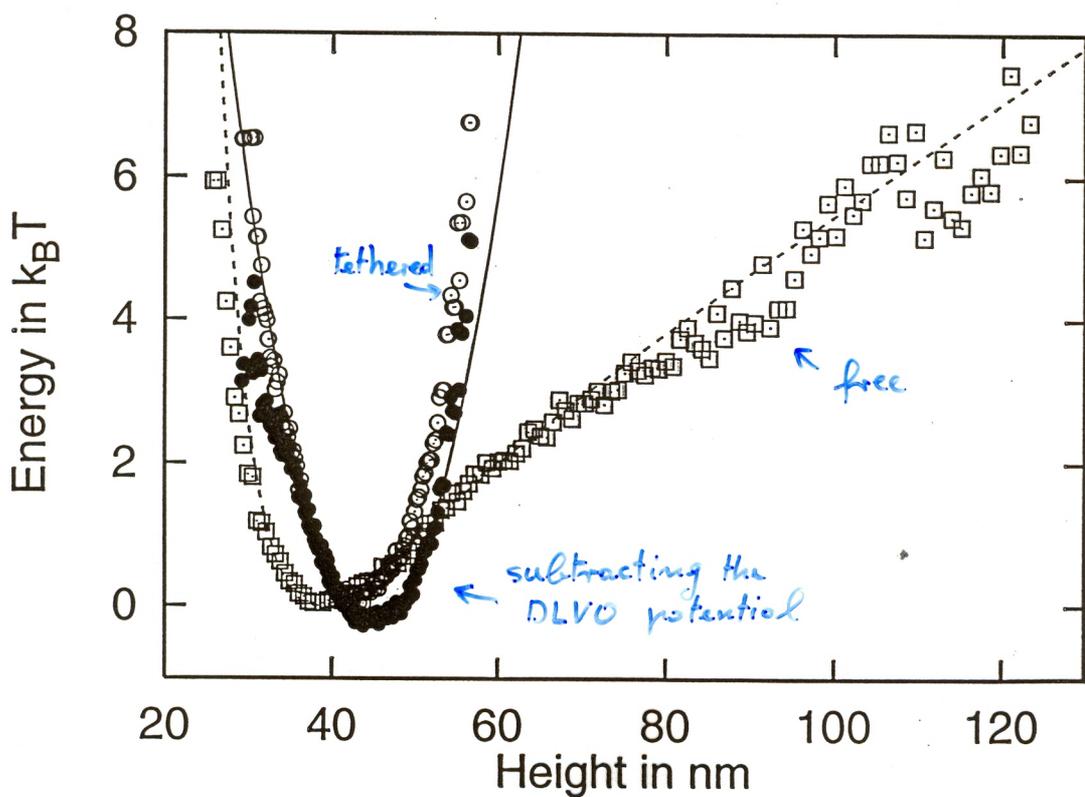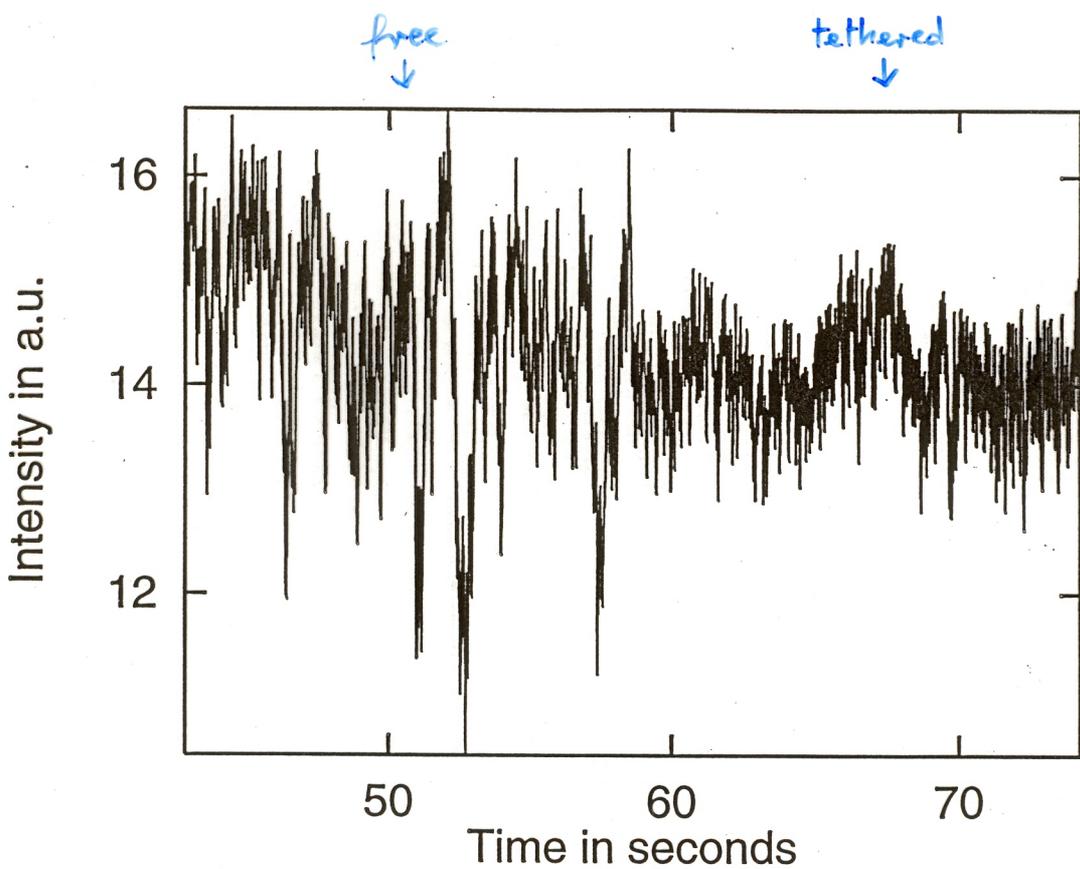
Polystyrene chain, 2% cross-linking

spring constant (from the measured potential)

$$K \simeq 1.5 \times 10^{-3} \ N/m$$

[Henriette Jensenius,
G.Z. PRL 79, 5030
1997]
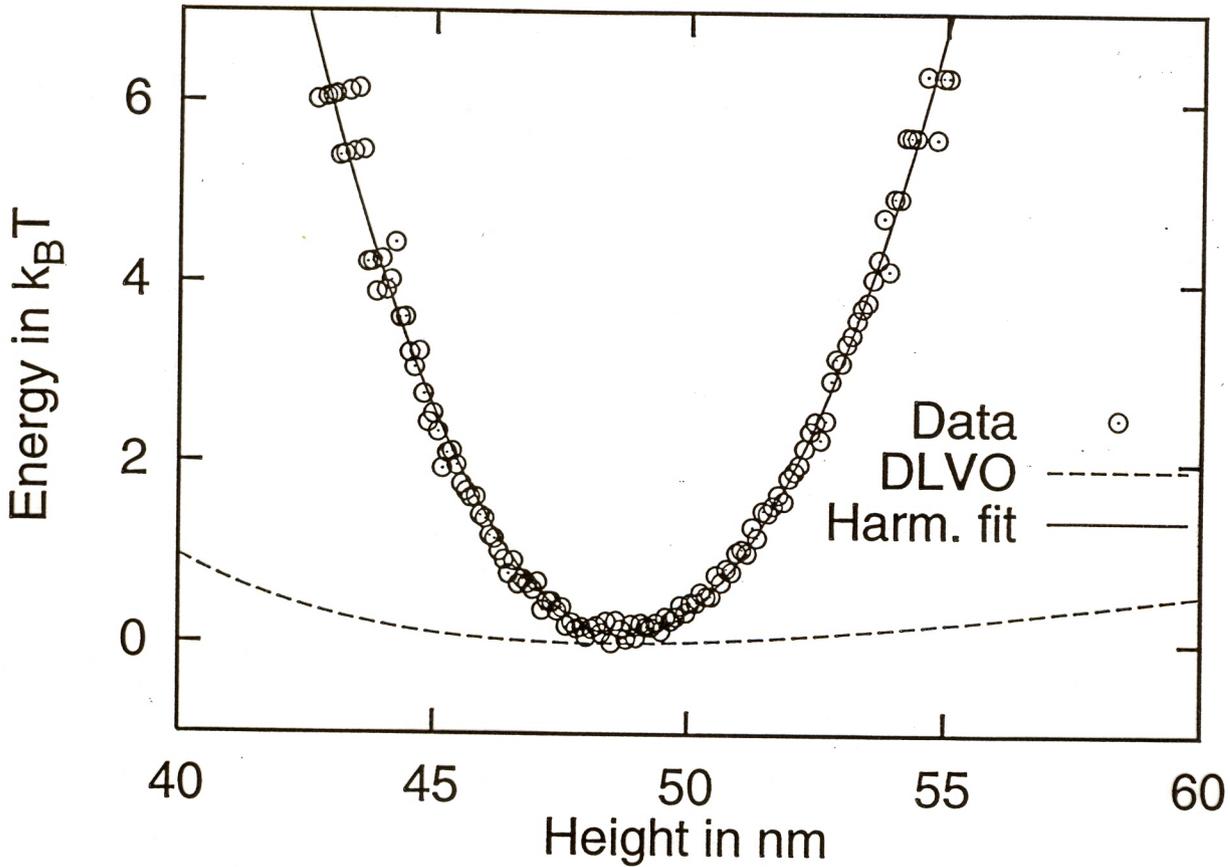
Spring constant of an ideal chain of size R :

$$K_{ideal} = \frac{3kT}{R^2} \quad ; \quad \text{for } R = 50 \ nm, \quad K_{ideal} \simeq 5 \times 10^{-6} \ N/m$$

With M_B cross-links : $\quad \dfrac{K_{cross-linked}}{K_{ideal}} = M_B$

Experiment: $\quad N_m \simeq 10^4$ (number of monomers), $\quad 2\%$ cross-linking

$$\Rightarrow M_B \simeq 200 \quad \Rightarrow K_{cross-linked} \simeq 10^{-3} \ N/m$$

Polystyrene chain ;   R ≃ 50 nm

A molecular (entropic) spring
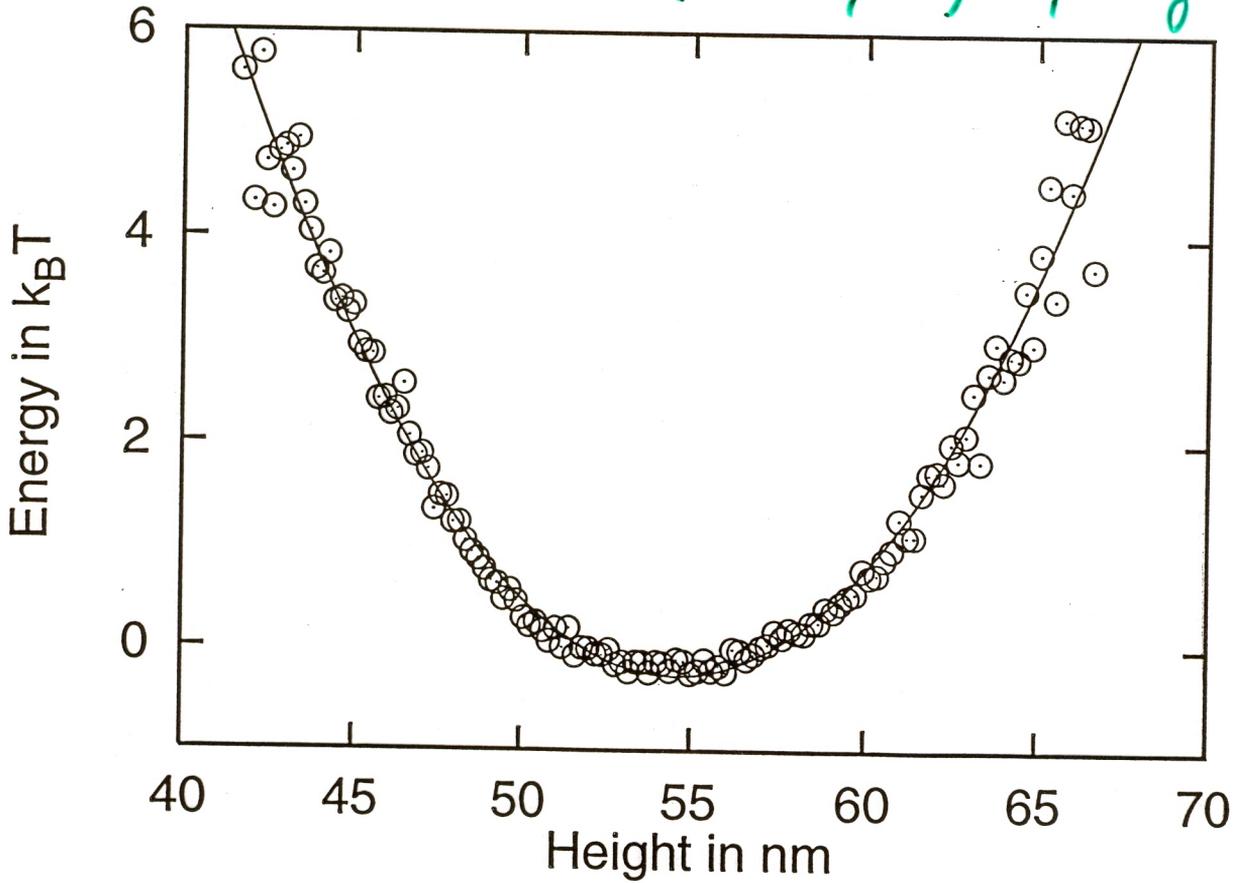
$K \simeq 2.9 \times 10^{-4}$ N/m .

i.e.   2 pN applied force ⟶ 6 nm displacement

(12% of the length of the spring.

Direct calculation of $\Gamma(\vec{R}) \propto e^{-\frac{3R^2}{2Nh^2}}$:

1-D :

N

r # steps to the right

l # " " \ left
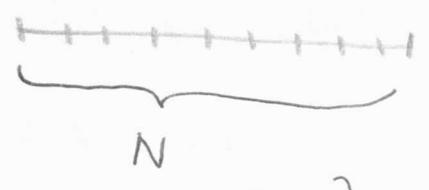
$r + l = N$;

$[n(r)]$ $N(r) = \dfrac{N!}{r! \, l!} = \dfrac{N!}{r! \, (N-r)!} = \dbinom{N}{r}$

$\left. \begin{array}{l} X = r - l \\ N = r + l \end{array} \right\}$ $\Rightarrow$ $\left. \begin{array}{l} r = \dfrac{N+X}{2} \\ l = \dfrac{N-X}{2} \end{array} \right\}$

$\Rightarrow$ $N(x) = \dfrac{N!}{\left(\dfrac{N+X}{2}\right)! \left(\dfrac{N-X}{2}\right)!}$

number of walks which were back displaced by x .

Note : $N(x)$ is max for $X = 0$ $\rightarrow$ the longest

number of states is for the random walk to come back to itself .

$\longrightarrow$

Stirling approx. : $\ln(M!) \simeq n \ln n - n$

$(\Leftarrow)$ $M! = n^M e^{-u} = \left(\dfrac{M}{e}\right)^n$ for $n \gg 1$

$\Rightarrow$ $N(x) \simeq \dfrac{(N/e)^N}{\left(\dfrac{N+X}{2e}\right)^{\frac{N+X}{2}} \left(\dfrac{N-X}{2e}\right)^{\frac{N-X}{2}}}$ for $X \ll N$

Therefore :

(polymer exerts a stress on attachment points)

on the other hand, with free ends the eq. EED $\neq 0$

because :
$$P(\vec{R}) \propto e^{-3R^2/2\langle R^2\rangle}$$

but
$$P(R) \propto 4\pi R^2 e^{-3R^2/2\langle R^2\rangle}$$
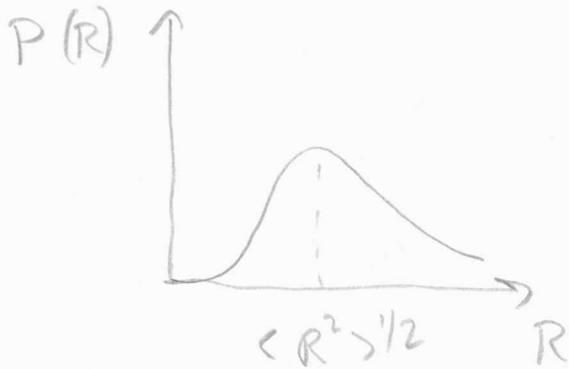
$$(2e)^{\left[\frac{N+x}{2} + \frac{N-x}{2}\right]} = (2e)^N \qquad etc.$$

$$\Rightarrow \quad N(x) \simeq \frac{(2N)^N}{(N+x)^{\frac{N+x}{2}} (N-x)^{\frac{N-x}{2}}} = \frac{2^N}{\left(1+\frac{x}{N}\right)^{\frac{N+x}{2}} \left(1-\frac{x}{N}\right)^{\frac{N-x}{2}}}$$

$$\Rightarrow \quad \ln N(x) = N\ln 2 - \frac{N+x}{2} \ln\left(1+\frac{x}{N}\right) - \frac{N-x}{2} \ln\left(1-\frac{x}{N}\right)$$

use $\ln(1+\alpha) \simeq \alpha - \frac{\alpha^2}{2}$ (have to keep second order to be consistent)

$$\Rightarrow \quad \ln N(x) \simeq N\ln 2 - \frac{N+x}{2}\left(\frac{x}{N} - \frac{x^2}{2N^2}\right) - \frac{N-x}{2}\left(-\frac{x}{N} - \frac{x^2}{2N^2}\right)$$

$$\simeq N\ln 2 - \frac{x^2}{4N} - \frac{x^2}{4N} = N\left[\ln 2 - \frac{x^2}{2N^2}\right]$$

$$\Rightarrow \quad N(x) \simeq 2^N e^{-\frac{x^2}{2N}} \qquad (x \ll N)$$

Since the tot. # of walks is 2^N, a better normalization

is:

$$\int_{-\infty}^{+\infty} e^{-x^2} dx = \sqrt{\pi} \qquad \left[\int e^{-(x^2+y^2)} dx\,dy \right.$$

$$\Rightarrow \quad \int_{-\infty}^{+\infty} e^{-\frac{x^2}{2N}} dx = \sqrt{2\pi N} \qquad = \int_0^\infty e^{-r^2} 2\pi r\, dr = \pi \left. etc. \right]$$

So $\quad N(x) = \frac{1}{(2\pi N)^{1/2}} 2^N e^{-\frac{x^2}{2N}}$ normalized.

2^N is the cond. number

3-D :
$$N(\vec{R}) \propto e^{-\frac{3R^2}{2N}}$$

(see p5$\frac{x}{8}$ for the factor of 3)

and the number of walks with

$$EED = |\vec{R}| = R \quad is \quad :$$

$$N(R)\, dR \propto N(\vec{R}) \quad 4\pi R^2 dR$$

↑ number of walks reaching a specific point $\vec{R}$ (at distance R)

↖ number of points at distance R   (3-D)

$$\Rightarrow \quad N(R) \propto 4\pi R^2 e^{-\frac{3R^2}{2N}} \quad ;$$

including the normaliz. and the coord. number :

$$N(R) = \frac{c^N}{(2\pi N)^{3/2}} \; 4\pi R^2 e^{-\frac{3R^2}{2N}}$$

(if you want to put back in $\hbar$:

$R \rightarrow R/\ell_K$ in this formula)

Note : C does not enter in any of the moments (e.g. $\langle R^2 \rangle$ etc.)

because $P(R) = \dfrac{N(R)}{c^N}$ since the tot. number of walks is c^N .

In summary :   the statistics of the single random walk is Gaussian _

Self-avoiding walks (SAWS):

physical system: real polymer (Flory theory)

final result: the polymer swells compared to the ideal
chain, and now $R \propto N^{3/5}$ instead of $N^{1/2}$.

real polymer: $\qquad c \to c-1$;

phase space reduction factor $\qquad x = 1\left(1 - \frac{v}{V}\right)\left(1 - \frac{2v}{V}\right) \cdots$

$V = R^3$, $\qquad R$ size of the coil $\qquad \cdots \left[1 - \frac{(N-1)v}{V}\right]$

v volume of one monomer

$$x = \frac{v^N}{V^N} \frac{V}{v}\left(\frac{V}{v} - 1\right)\left(\frac{V}{v} - 2\right) \cdots \left[\frac{V}{v} - (N-1)\right]$$

$$\Rightarrow \quad x = \frac{v^N}{V^N} \frac{(V/v)!}{\left(\frac{V}{v} - N\right)!} \approx \frac{v^N}{V^N} \frac{(V/v)^{V/v} \, e^{-V/v}}{\left(\frac{V}{v} - N\right)^{\frac{V}{v} - N} e^{-\left(\frac{V}{v} - N\right)}}$$

$$= e^{-N}\left(\frac{V/v}{V/v - N}\right)^{\frac{V}{v} - N} \qquad\qquad \left(\text{for } \frac{V}{v} \gg N\right.$$

$$\left. \Rightarrow Nv \ll V \right)$$

with $\quad x := \frac{N}{V/v} \qquad (\Rightarrow x \overset{<<}{\sim} 1)$

$$\Rightarrow \frac{V}{v} = \frac{N}{x} , \quad \frac{V}{v} - N = N\left(\frac{1}{x} - 1\right)$$

and $\quad x = e^{-N} \left[\dfrac{N/x}{N\left(\frac{1}{x}-1\right)} \right]^{N\left(\frac{1}{x}-1\right)}$

$= e^{-N} \left[\dfrac{1}{1-x} \right]^{\frac{1}{x}\left(N - \frac{N^2}{v/v}\right)} \qquad = e^{-N} (1-x)^{-\frac{1}{x}\left(N - \frac{N^2}{v/v}\right)}$

now $\quad \lim_{x \to 0} (1-x)^{-\frac{1}{x}} = e \qquad$ so $\quad x \to e^{-\frac{N^2}{v/v}}$

or $\quad x = e^{-\frac{N^2 v}{R^3}} \qquad\qquad R$ is radius of gyration

Now the number of walks with $EED = R$ is :

$$N(R) = \dfrac{c^N}{(2\pi N)^{3/2}} \, 4\pi \left(\dfrac{R}{l_k}\right)^2 e^{-\frac{3(R/l_k)^2}{2N}} \; e^{-v\frac{N^2}{R^3}}$$

What is the R which maximizes N ?

$\dfrac{\partial N}{\partial R} = 0 \qquad (\to$ ignore factors indep. of R)

$\Rightarrow \quad \dfrac{2R}{l_k^2} + \left(\dfrac{R}{l_k}\right)^2 \left[-\dfrac{3R}{N l_k^2} + 3\dfrac{v N^2}{R^4} \right] = 0$

$\Rightarrow \quad \dfrac{2}{R} - \dfrac{3R}{N l_k^2} + 3\dfrac{v N^2}{R^4} = 0$

For large N, the first term is small
(see later) $\longrightarrow$ $R^5 \approx v \ell_k^2 N^3$

$\Rightarrow$ $R \approx (v \ell_k^2)^{1/5} N^{3/5}$ (Flory scaling)

consistent because if $R \propto N^{3/5}$, then the

2nd & 3rd terms in the eq. are both $\propto \dfrac{1}{N^{4/5}}$

but the 1st term is $\propto \dfrac{1}{N^{3/5}}$ —

This was to show that the physics here is just counting the number of states —

Free energy way of doing this (you do the same : it's just fancy counting) :

effective monomer – monomer interaction :
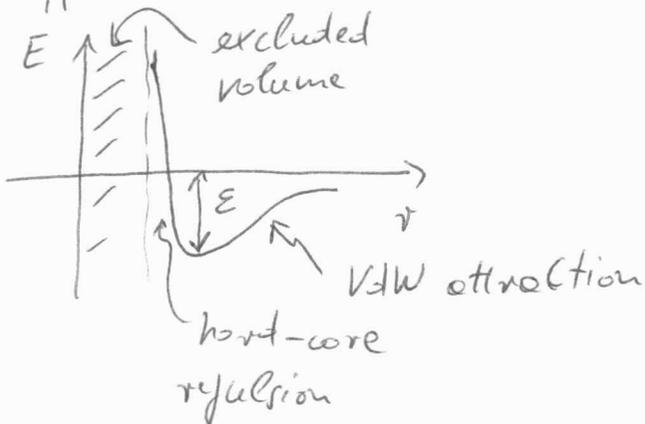
$E \gg kT \longrightarrow$ collapse (bad solvent)

$E \ll kT \longrightarrow$ swelling (entropic ; good solvent)
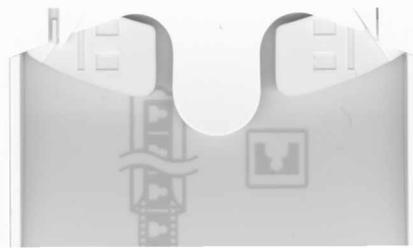
Swelling in good solvents :

mathematically, the picture is that of a ~~self~~ self - avoiding random walk — But on SAW s, you can do only numerics —

You find $R_F = \ell N^{\nu}$ with $\nu = 0.6$ $\longrightarrow$

<u>Flory calculation</u> :

> balance the excluded volume (repulsive) interaction with the elastic (entropic) restoring force —

Repulsive interaction : $c = \dfrac{N}{V}$ monomer conc. is "small"

$\left[\phi = \dfrac{N v}{V} \ll 1 \quad \text{volume fraction} \right]$ V volume of the coil

$$V \sim R^3 \quad \longrightarrow$$

expand F_{rep} in powers of c : $F_{rep} = V kT \left[A_2 c^2 + A_3 c^3 \right.$

A₂ second virial coeff. $\left. + \cdots \right]$

A_2 second virial coeff.

2 body interactions , 3 body int., etc —

$A_2 > 0$ (high T, good solvent) $\longrightarrow$ swelling

$A_2 < 0$ (low T, bad solvent) $\longrightarrow$ collapse

$A_2 = 0$: θ point $F_{rep} \simeq 0 \longrightarrow$ ideal chain

(interactions cancel out ; how can you get back an ideal chain ? Because there is still a physical excluded volume ! But see later ; this is an entropic effect : a slight attractive interaction can cancel out the physical excluded volume)

Note : this is not a small difference

$$(100)^{0.5} = 10 \quad \text{but} \quad (100)^{0.6} = 16 \quad !$$

you are saying : the "small parameter" is c ;

$\dfrac{F}{V}$ is a function of c etc.

First. (introction) better notation

Swelling $(A_2 > 0)$: $\quad F_{rep.} = R^3 kT A_2 \left(\frac{N}{R^3}\right)^2$

$\Rightarrow \quad F_{rep.} = NkT \dfrac{N A_2}{R^3}$ $\qquad$ note : $[A_2]$ = volume

Elastic restoring energy : $\quad F_{el} = \dfrac{3kT}{2R_0^2} R^2$ $\quad \boxed{\begin{array}{l} R_0^2 = N\ell_K^2 \\ \text{Kuhn length} \uparrow \end{array}}$

$\Rightarrow \quad F = F_{rep.} + F_{el} = kT\left[\dfrac{N^2 A_2}{R^3} + \dfrac{3R^2}{2N\ell^2}\right] \quad \longrightarrow$

Maximize F : $\quad \dfrac{\partial F}{\partial R} = 0 \quad$ for $\quad R_F = \ell N^{3/5}\left(\dfrac{A_2}{\ell^3}\right)^{1/5}$

i.e. $\quad R_F \sim \ell N^\nu \quad$ with $\quad \nu = \dfrac{3}{5} \qquad$ Flory exponent

— Note of R vs N scaling —

Alternative derivation $\overset{\text{for Flul.}}{:}$ $\qquad \nu \quad$ volume occupied by one monomer

what is the entropic cost of having a non zero ν ?

$\Delta S = k \ln \Gamma(\nu) - k \ln \Gamma(\nu=0) = k \ln \dfrac{\Gamma(\nu)}{\Gamma(\nu=0)}$

$\Gamma(\nu=0) \propto (R^3)^N$; $\quad \Gamma(\nu) \propto (R^3 - N\nu)^N \quad \longrightarrow$

$\Rightarrow \quad \Delta S = Nk \ln \dfrac{R^3 - N\nu}{R^3}$; $\quad \ln\left(1 - \dfrac{N\nu}{R^3}\right) \simeq -\dfrac{N\nu}{R^3}$

$\left(\dfrac{N\nu}{R^3} \ll 1\right) \Rightarrow \Delta S = -Nk\dfrac{N\nu}{R^3} \quad F_{rep}$

$A_2 > 0$ means repulsion $\quad$ (F goes up if
$\qquad\qquad\qquad\qquad\qquad\qquad$ C is increased)

$\Gamma(v) \propto (R^3 - Nv)^N \quad$ is approximate :

1) valid only for $\quad Nv \ll R^3$

2) it neglects correlations (the fact that the monomers
are all linked in a chain) :

example : $\qquad$ 9 sites , $N = 5$ "polymer"
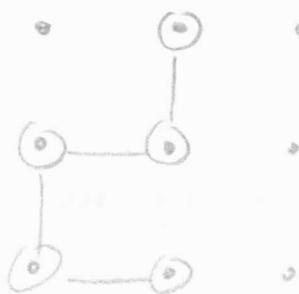
one
config.

Without the requirement
of a linked chain :

$$\Gamma = 9 \times 8 \times 7 \times 6 \times 5$$

our approx. : $\quad \Gamma \simeq (9-5)^5 = 4^5$

actual # states for a linked, self-avoiding
chain = ? $\qquad$ (Put it on a computer)
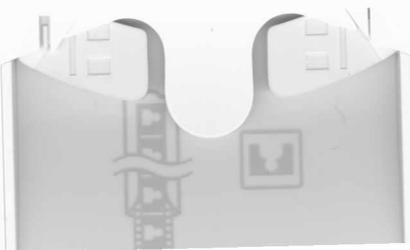
$$\Rightarrow \quad F_{rep.} = NkT \frac{Nv}{R^3}$$

[What is the meaning of $v < 0$? Why is the entropy increased ?
Because a monomer spends more time close to another monomer, as
if it had been swallowed by some extra volume in phase space;
$v = 0$ when this "extra volume" balances the actual
excluded volume :
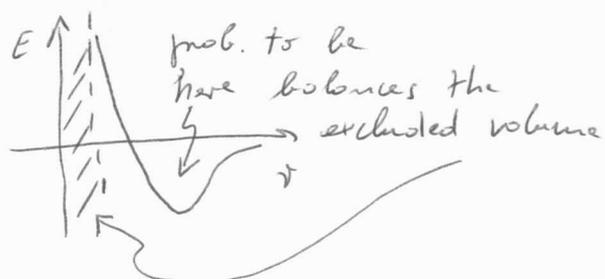
In d dimensions $= \quad V \sim R^d \quad$ volume of the coil

$$\Rightarrow \quad \Delta S = - \frac{Nv}{R^d} \quad \Rightarrow \quad F_{rep} = NkT \frac{Nv}{R^d}$$

$$\Rightarrow \quad R_F \sim N^v \quad \text{with} \quad v = \frac{3}{d+2}$$

essentially exact for $d = 1, 2, 3, 4$.

Polymer collapse :   (solvent effects)

re-parametrize the monomer-monomer interaction, separating the excluded volume out a longer range interaction :
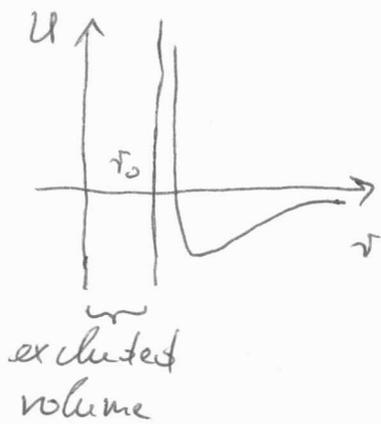
excluded
volume

$$\mathcal{E} = - \int_{r_0}^{\infty} d^3x \; U \qquad [\mathcal{E}] = \text{energy} \times \text{volume}$$

$\mathcal{E} > 0$ means attraction ($\rightarrow$ collapse)

$\rightarrow$ this part of the monomer-monomer interaction is

$$\propto \int d^3x \; \rho U = -\rho \mathcal{E}$$

with $\rho = \dfrac{N}{V}$ mean field monomer density

free energy : $F(R) = E - TS = -\dfrac{1}{2}\rho \mathcal{E} N - kT \ln N(R)$

N includes excluded volume effects

$\dfrac{1}{2}$ takes care of double counting

$\left(\; S(R) = k \ln [N(R)] \; \right)$

$$N(R) = \frac{C^N}{(2\pi N)^{3/2}} \; 4\pi \left(\frac{R}{\ell_K}\right)^2 e^{-\frac{3(R/\ell_K)^2}{2N}} \quad \chi$$

$$\chi = e^{-N} \left(\frac{V/v}{V/v - N}\right)^{\frac{V}{v} - N}$$

(can't simply use
$\chi \sim e^{-\frac{N^2 v}{R^3}}$ because
this is o.k. for $\dfrac{N}{V/v} \ll 1$ $\Rightarrow$)

For F we need $\ln X$:

$$X = e^{-N} \left(\frac{V/v - N}{V/v} \right)^{N - \frac{V}{v}}$$

$$\Rightarrow \quad \ln X = -N + \left(N - \frac{V}{v} \right) \ln \left(1 - \frac{Nv}{V} \right)$$

expand $\ln$ to 3d order in $\frac{Nv}{R^3} < 1$:

(i.e. keep 3-body interactions)

$$\ln (1+x) \simeq x - \frac{x^2}{2} + \frac{x^3}{3} \qquad so \quad =$$

$$\ln X \sim \left(N - \frac{V}{v} \right) \left[- \frac{Nv}{V} - \frac{1}{2} \left(\frac{Nv}{V} \right)^2 - \frac{1}{3} \left(\frac{Nv}{V} \right)^3 \right]$$

$$\sim \quad - \frac{N^2 v}{2 R^3} - \frac{1}{6} \frac{v^2 N^3}{R^6} \qquad \left(\begin{array}{l} \text{keeping only } R\text{-dep.} \\ \text{terms ; also tossing} \\ \text{the } N^4 \text{ term which} \\ \text{would be 4-body int.} \end{array} \right)$$

So $\quad \dfrac{F}{T} \sim \dfrac{1}{2} \left(v - \dfrac{\varepsilon}{T} \right) \dfrac{N^2}{R^3} + \dfrac{3R^2}{2 \ell_k^2 N} + \dfrac{1}{6} \dfrac{N^3 v^2}{R^6} - 2 \ln \dfrac{R}{\ell_k}$

(only R dep. terms)

$v \dfrac{N^2}{R^3} = $ excluded volume term, repulsive (two-body)

$\dfrac{\varepsilon}{T} \dfrac{N^2}{R^3} = $ monomer-mon. int. term (repulsive or attraction)

$\dfrac{3R^2}{2\ell_k^2 N} - 2 \ln \dfrac{R}{\ell_k} = $ entropy of configurations associated with the EED R
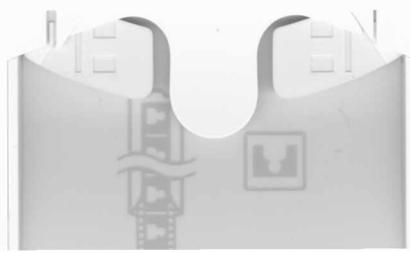
$$N \frac{N^2}{R^6} v^2 = \qquad 3\text{-body repulsive "hard core";}$$

necessary otherwise $R \to 0$ upon collapse

a) $\quad 1 - \frac{\varepsilon}{vT} > 0 \qquad :$ in terms of $\theta = \frac{\varepsilon}{v}$ theta temp.

(temp. where $A_2 = 0$)

this is $\boxed{T > \theta}$ good solvent

i.e. net monomer-monomer repulsion

Then the polymer is swollen, and

$$\frac{F}{T} \sim \frac{1}{2}\left(1 - \frac{\varepsilon}{vT}\right) v \frac{N^2}{R^3} + \frac{3R^2}{2 \ell_k^2 N}$$

$$\frac{\partial F}{\partial R} = 0 \quad \text{gives} \quad -\frac{N^2}{R^4} \sim -\frac{R}{N} \quad \text{i.e.} \quad R \sim N^{3/5}$$

b) $\quad 1 - \frac{\varepsilon}{vT} = 0 \qquad$ i.e. $T = \theta \qquad$ "Theta point"

polymer is still an expanded coil

$$\to \quad F/T \sim \frac{3R^2}{2\ell_k^2 N} - 2 \ln \frac{R}{\ell_k}$$

$$\frac{\partial F}{\partial R} = 0 \quad \Rightarrow \quad \frac{3R}{\ell_k^2 N} - 2/R = 0 \quad \Rightarrow \quad R^2 = \frac{2}{3} \ell_k^2 N$$

or $R \sim \ell_k N^{1/2} \qquad$ ideal chain !

(zero net monomer-monomer int.)

c) $1 - \frac{\varepsilon}{vT} < 0$ i.e. $T < \Theta$ → collapse

re-parametrize $R = \alpha \, \ell_K \, N^{1/2}$ α "swelling parameter"

$\alpha = \alpha(N)$: $\alpha > 1$: swelling

$\alpha < 1$: collapse

So $\frac{F}{T} \sim \frac{1}{2}\left(v - \frac{\varepsilon}{T}\right) \frac{N^{1/2}}{\ell_K^3 \, \alpha^3} + \frac{3}{2}\alpha^2 + \frac{1}{6}\frac{v^2}{\ell_K^6 \, \alpha^6} - 2\ln(\alpha \, N^{1/2})$

$X := \frac{1}{2}\left(v - \frac{\varepsilon}{T}\right)\frac{N^{1/2}}{\ell_K^3}$ in terms of $\Theta = \frac{\varepsilon}{v}$

$\underbrace{}_{\sim A_2}$

$v - \frac{\varepsilon}{T} = v\left(1 - \frac{\Theta}{T}\right) = v\,\frac{T-\Theta}{T}$

$\propto T - \Theta$

(i.e. $A_2 > 0$ above Θ, $A_2 < 0$ below Θ)

So $X = \frac{1}{2} v \, \frac{T-\Theta}{T} \, \frac{N^{1/2}}{\ell_K^3}$

$y := \frac{1}{6}\frac{v^2}{\ell_K^6}$ ($\sim A_3$: 3-body inter.)

So $\frac{F}{T} \sim \frac{X}{\alpha^3} + \frac{3}{2}\alpha^2 + \frac{y}{\alpha^6} - 2\ln\alpha$

(dropping the N-dep. which is not important)

$$\frac{\partial F}{\partial \alpha} = 0 = \qquad X = \alpha^5 - \frac{2y}{\alpha^3} - \frac{2}{3} \alpha^3 \qquad (*)$$

Collapse: $\alpha \ll 1$ so $\alpha^3 \sim -\frac{2y}{X} = \frac{1}{3} \frac{v}{l_n^3} \frac{T}{\theta - T} N^{-1/2}$

$(T < \theta)$

or $R \simeq \left(\frac{v}{3} \frac{T}{\theta - T} \right)^{1/3} N^{1/3} \qquad \alpha \quad N^{1/3} \qquad$ compact!

For some values of y (and $x < 0$ i.e. $T < \theta$)

the $(*)$ has 3 solutions (instead of 1)

i.e. F has 3 extrema (2 min, 1 max);

similar to isotherms in the P-V plane of a VdW gas:

Here:
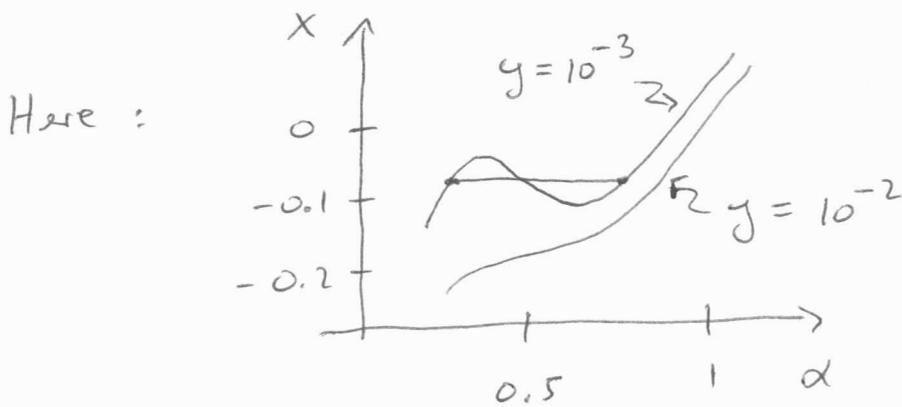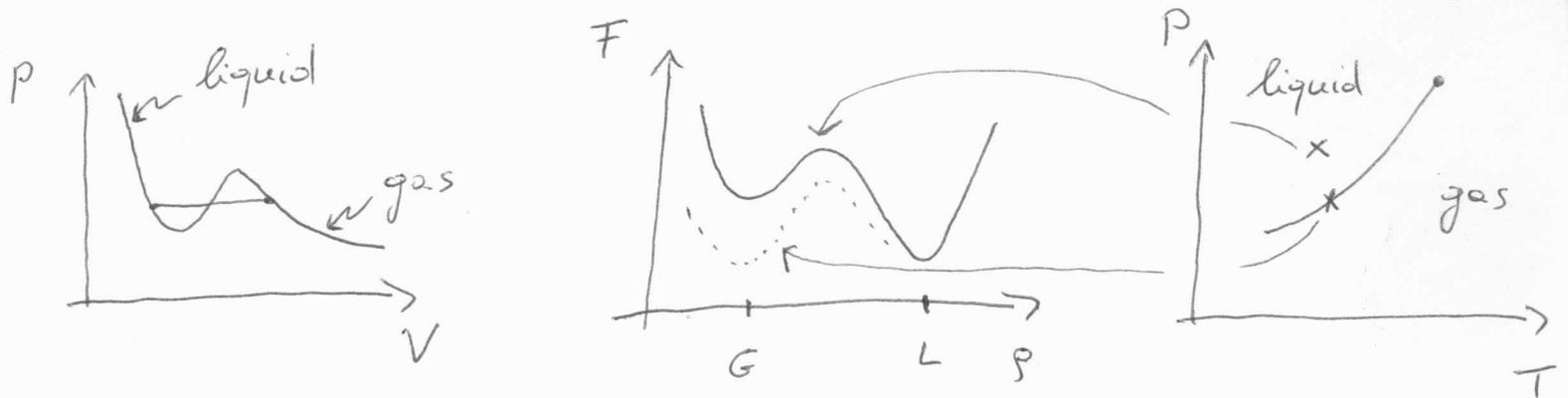
i.e. for y sufficiently small and $x < 0$

$(T < \theta)$

$\rightarrow$ 1st order phase transition.

$\longrightarrow$

so = 1st order $\cancel{\text{first}}$ phase transition

for y small (ℓ_k large : stiff chain)

and v small = large persistence length,

small excluded volume —