3. Beyond the Freely Jointed Chain

Are the results from the FJC in agreement with experiments?

No! As measured, the exponent ν that is found for polymers is

$\tilde{R}_{ee} \sim b N^{\nu}$, with

d	ν	
2	0.75 (± ...)	$\longrightarrow$ simulations + exact solution $3/4$
3	0.6 (± ...)	$\longrightarrow$ numerical simulations give 0.588...

We will discuss computational and analytical results later.

It is clear then that the FJC is not appropriate to describe real polymers (nonetheless, there are cases where it can be used in very instructive ways).

Let's get back to the fundamental equation:

$$\tilde{R}_{ee}^{2} = \langle \vec{R}_{ee}^{2} \rangle = \underbrace{b^2 N}_{} + \underbrace{2 \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \langle \vec{r}_j \cdot \vec{r}_i \rangle}_{}$$

is the same for any model

$\Downarrow$

provides $\nu = 1/2$

corrections to the exponent can only come from this part, namely, from correlations between different segments along the polymer.

How can we introduce correlations? We need $\langle \vec{r}_j \cdot \vec{r}_i \rangle \neq 0$

We recall that in physics averages must be computed from physically motivated probability distributions à la Boltzmann

$$p(\{\vec{r}_i\}) = \frac{1}{Z} e^{-\beta U(\{\vec{r}_i\})}$$

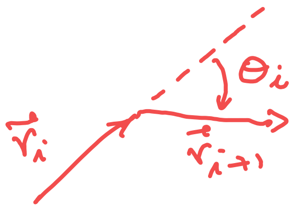
What is the simplest complication of the FJC?

FJC: no interactions between any pair of bonds

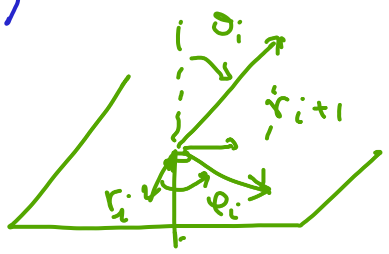
We introduce the Kratky-Porod model, where interactions are present only between consecutive bonds:

$$U(\{\vec{r}_i\}) = \sum_{i=1}^{N-1} u(\vec{r}_{i+1}, \vec{r}_i)$$

We can then simply see that, whatever the direction of $\vec{r}_i$, the only relevant information is the direction of $\vec{r}_{i+1}$ relative to $\vec{r}_i$:



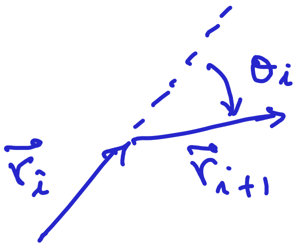
and as a consequence $u(\vec{r}_{i+1}, \vec{r}_i) = u(\theta_i)$



[here we neglect the equatorial angle φ_i because, for infinitely thin and axially isotropic bond, it is of no relevance. Of course it has relevance for real polymers, but not for now]

Given that each vector is of fixed length, the complete conformation is determined by: the first vector, and then the relative orientation of each vector with respect to the previous one.

Let's start in two dimensions



We can thus compute

this is computed relative to an arbitrary reference → $d\theta_0$

$$\langle \vec{r}_{i+1}\cdot\vec{r}_i\rangle = \frac{1}{Z}\int \overbrace{d\vec{r}_1}\int_0^{2\pi} d\theta_1 \int_0^{2\pi} d\theta_2 \cdots \int_0^{2\pi} d\theta_{N-1}\,\underbrace{(\vec{r}_{i+1}\cdot\vec{r}_i)}\,e^{-\beta\sum_{i=1}^{N-1}u(\theta_i)} =$$

$$= \overbrace{b^2}\,\frac{1}{Z}\underbrace{\int_0^{2\pi} d\theta_0}\;\underbrace{\int_0^{2\pi} d\theta_1\, e^{-\beta u(\theta_1)}}\cdots\underbrace{\int_0^{2\pi} d\theta_{i-1}\, e^{-\beta u(\theta_{i-1})}}\left[\int_0^{2\pi} d\theta_i\, \overbrace{\cos\theta_i}\, e^{-\beta u(\theta_i)}\right]$$

$$\cdots\underbrace{\int_0^{2\pi} d\theta_{N-1}\, e^{-\beta u(\theta_{N-1})}} =$$

$$= b^2\,\frac{1}{Z}\,\overbrace{2\pi}\;z_1\cdot z_2\cdots z_{i-1}\left[\int_0^{2\pi} d\theta_i \cos\theta_i\, e^{-\beta u(\theta_i)}\right] z_{\theta_{N-1}}$$

We can also compute Z :

$$Z = \int d\vec{r}_1 \int d\theta_1 \int d\theta_2 \cdots \int d\theta_{N-1}\; e^{-\beta\sum_{i=1}^{N-1} u(\theta_i)} =$$

$$= 2\pi\, z_1 z_2 \cdots z_{N-1}$$

and as a consequence we have

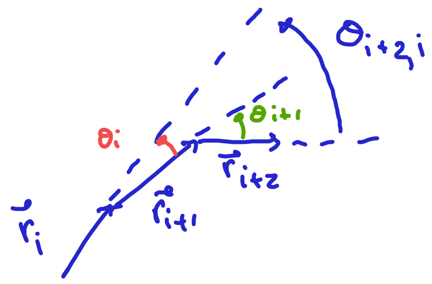
$$\langle \vec{r}_{i+1}\cdot\vec{r}_i\rangle = b^2\,\frac{2\pi z_1\cdots z_{i-1}\left[\int_0^{2\pi} d\theta_i\, e^{-\beta u(\theta_i)}\cos\theta_i\right] z_{i+1}\cdots z_{N-1}}{2\pi z_1\cdots\cdots z_{N-1}} =$$

$$= b^2\,\frac{1}{z_i}\int_0^{2\pi} d\theta_i\, e^{-\beta u(\theta_i)}\cos\theta_i = b^2\,\underbrace{c_i}_{c_i\leq 1} = \langle\cos\theta_i\rangle\, b^2$$

because $|\cos\theta_i| \leq 1$

As an approximation, say $c_i = c \quad \forall i$

What about $\langle \vec{r}_{i+2} \cdot \vec{r}_i \rangle$?



$$\Longrightarrow \qquad \theta_{i+2,i} = \theta_{i+1} + \theta_i$$

$$\vec{r}_{i+2} \cdot \vec{r}_i = b^2 \cos(\theta_{i+2,i}) = b^2 \left[\cos(\theta_{i+1}) \cos(\theta_i) - \sin(\theta_{i+1}) \sin(\theta_i)\right]$$

We can then compute

$$\langle \vec{r}_{i+2} \cdot \vec{r}_i \rangle = b^2 \langle \cos(\theta_{i+2,i}) \rangle = b^2 \{ \langle \cos(\theta_{i+1}) \cos(\theta_i) \rangle +$$

$$- \langle \sin(\theta_{i+1}) \sin(\theta_i) \rangle \} =$$

$$= b^2 \{ \underbrace{\langle \cos(\theta_{i+1}) \rangle \langle \cos(\theta_i) \rangle} - \underbrace{\langle \sin(\theta_{i+1}) \rangle \langle \sin(\theta_i) \rangle} \}$$

here we used the fact that $e^{-\beta \sum_i u(\theta_i)} = \prod_i e^{-\beta u(\theta_i)}$
so that the angles $\{\theta_i\}$ are independent.

We next add the simplification that $u(\theta) = u(-\theta)$

$\Longrightarrow \quad \langle \sin\theta \rangle = 0 \qquad$ (integral of an odd function)

and we finally get

$$\langle \vec{r}_{i+2} \cdot \vec{r}_i \rangle = b^2 c^2$$

We can go on and show

$$\langle \vec{r}_j \cdot \vec{r}_i \rangle = b^2 c^{|j-i|} = b^2 c^{\overset{\swarrow \text{ if } j>i}{(j-i)}}$$

We thus have :

$$\langle \vec{R}_{ee}^{\,2} \rangle = b^2N + 2b^2\sum_{i=1}^{N-1}\sum_{j=i+1}^{N} c^{j-i} =$$

$$= b^2N + 2b^2 \sum_{i=1}^{N-1}\underset{\substack{\uparrow \\ \text{change of} \\ \text{variable : } k=j-i}}{\sum_{k=1}^{N-i}} c^k = b^2N + 2b^2\sum_{i=1}^{N-1}\underbrace{\left(\frac{1-c^{N-i+1}}{1-c} - 1\right)}_{\text{recall that } \sum_{k=0}^{M} c^k = \frac{1-c^{M+1}}{1-c}} =$$

$$= b^2N + 2b^2\left[\sum_{i=1}^{N-1}\frac{c-c^{N-i+1}}{1-c}\right]$$

same here

$$= b^2N + 2b^2(N-1)\frac{c}{1-c} - 2b^2\frac{c^{N+1}}{1-c}\underline{\sum_{i=1}^{N-1}\left(\frac{1}{c}\right)^i} =$$

$$= b^2N\,\frac{1+c}{1-c} - 2b^2\frac{c}{1-c} - 2b^2\frac{c^{N+1}}{1-c}\left(\frac{\frac{1}{c} - \left(\frac{1}{c}\right)^N}{1 - 1/c}\right)$$

$$= \frac{1+c}{1-c}\,b^2N - 2b^2\frac{c}{1-c} + 2b^2\frac{c^N - c}{\frac{1}{c}\,(1-c)^2} =$$

$$= \frac{1+c}{1-c}\,b^2N - 2b^2\frac{c}{1-c} - 2b^2c\,\frac{c-c^N}{(1-c)^2}$$

Let us first look at long polymers : $N \gg 1$

since $|c| < 1 \Rightarrow c^{N-1} \longrightarrow 0$ exponentially and

$$\langle \vec{R}_{ee}^{\,2} \rangle \simeq \frac{1+c}{1-c}\,b^2N - 2b^2\frac{c}{1-c}\left(1 + \frac{c}{1-c}\right) = \frac{1+c}{1-c}\,b^2N - 2b^2\frac{c}{(1-c)^2}$$

The main message of this result is that introducing correlations through a local interaction $u(\theta)$ does not change the scaling behavior $\nu = 1/2$ [Lexicon: "scaling behavior" is used when the relation between two quantities is algebraic:

$$A \sim B^{\alpha}$$]

On the one hand, this means that the origin of the correction to the exponent ν, that we know comes from

$$\sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \langle \vec{r}_i \cdot \vec{r}_j \rangle$$

is subtler than previously believed.

On the other hand, this result also gives us the chance to look at the Kratky-Porod model in a different way.

Rescaling of the KP model

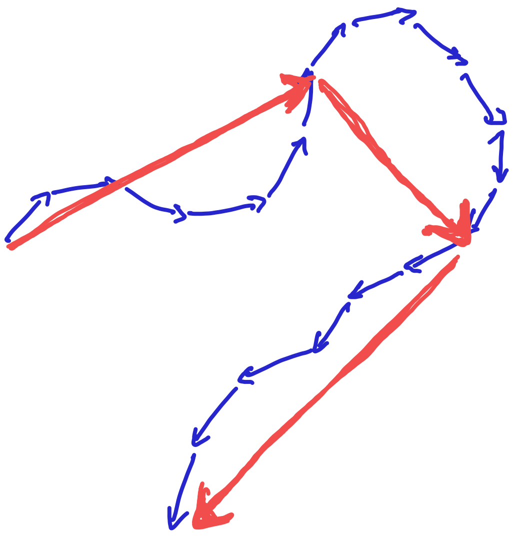
At leading order, when $N \gg 1$, $\langle \vec{R}_{ee}^{\,2} \rangle \simeq \frac{1+c}{1-c} b^2 N$

If it were a FJC, it would be $\langle \vec{R}_{ee}^{\,2} \rangle = \ell_K^2 N$, with ℓ_K the length of the independent vectors.

So, can we "rescale" the KP model to make it look like a FJC?

! Important: when you perform a rescaling of the microscopic degrees of freedom, you are changing your own representation of the system. Reality does not depend on the representation, and as a consequence there are constraints given by measurable quantities.

Pictorially:



KP model with local rigidity (consecutive vectors are in general pretty much aligned)

The idea of the rescaling is to define new vectors, of length l_k, and of number N', so that

$$\langle \vec{R}_{ee}^{\,2} \rangle \simeq l_k^2 N'$$

How do we determine l_k and N'?

① The total length is given:

$$bN = l_k N'$$

② $\langle \vec{R}_{ee}^{\,2} \rangle$ is measurable ⇒ real quantity

$$\frac{1+c}{1-c} b^2 N = l_k^2 N'$$

Solving the first constraint gives

$$N = \frac{l_k}{b} N'$$

plugging it in the equation for the second constraint gives

$$\frac{1+c}{1-c} b^2 \frac{l_k}{b} N' = l_k^2 N'$$

whose solution is

$$l_K = \frac{1+c}{1-c}\, b$$ (remember: $\frac{1+c}{1-c} > 1$ if, as expected $0 < c < 1$)

and

$$N' = \frac{1-c}{1+c}\, N$$

That is, the KP polymer is equivalent to a FJC polymer made of fewer segments ($N' < N$) of longer length ($l_K > b$). The length of the segments, l_K, is also called Kuhn length.

This is already an important result, because it allows using experiments to explore the mechanical properties of biomacromolecules. For exemple, measuring $\langle \vec{R}_{ee}^2 \rangle$ of long dsDNA as a function of the number of bases gives the opportunity to know its rigidity. Indeed, if the length of a basepair is b ($b \simeq 3\,\text{Å}$) then the length is

$$L = bN$$ $N = \#$ of basepairs

but $\langle \vec{R}_{ee}^2 \rangle \neq b^2 N$

we can thus define

$$l_K N' = L$$

$$l_K^2 N' = \langle \vec{R}_{ee}^2 \rangle_{\text{measured}}$$

to find

$$N' = \frac{L}{\ell_K}$$

and

$$\ell_K = \frac{\langle \vec{R}_{ee}^{\,2} \rangle_{measured}}{L}$$

(by the way, this is very appealing and comforting: the most appropriate rescaling emerges naturally from the measurements)

Interesting, $\ell_{K,\,dsDNA} \simeq 100$ nm $\Rightarrow$ about 300 bp

$\uparrow$

bp = basepair

<u>dsDNA is really very rigid!</u>

But

$$\ell_K = \frac{1+c}{1-c}\, b \quad \Rightarrow \quad \frac{1+c}{1-c} = \frac{\ell_K}{b}$$

$$\Rightarrow \quad \left(1 + \frac{\ell_K}{b}\right) c = \frac{\ell_K}{b} - 1 \quad \Rightarrow \quad c = \frac{\frac{\ell_K}{b} - 1}{\frac{\ell_K}{b} + 1}$$

Recalling that

$$c = \int d\theta \, \cos\theta \; e^{-\beta u(\theta)} \, , \quad \Leftarrow$$

careful: 2D formula (see later for 3D)

the measurements can give a clue about $u(\theta)$

We are going to look at this more in detail later in the course.

Let's see what "outstanding" questions remain to be addressed:

1) What happens when N is not $\gg 1$? What does it mean $N \gg 1$?
2) What happens for $d > 2$? Is φ (equatorial angle) irrelevant?
3) What happens in the continuum limit? What is the continuum limit?

1) N not $\gg 1$

Let's write again the formula:

$$\langle \vec{R}_{ee}^{\,2} \rangle = \frac{1+c}{1-c} b^2 N + 2b^2 \frac{c}{1-c} - 2b^2 c \frac{c - c^N}{(1-c)^2}$$

we have to work on c^N: we write it as $e^{N \ln c}$. Since $c < 1$ of course $\ln c < 0$ and we start understanding what $N \gg 1$ means:

$$e^{N \ln c} \ll 1 \quad \text{if} \quad N|\ln c| \gg 1$$

$$\Rightarrow \quad N \gg \frac{1}{|\ln c|}$$

we can define $\xi_p = \frac{1}{|\ln c|}$ as the persistence number of segments.

If $N \gg \xi_p$ then the polymer behaves as a FJC, otherwise (namely if N not $\gg \xi_p$) we must be more careful

If $\frac{N}{\xi_p} \lesssim 1$ then we can expand the exponential to second order

$$e^{N/\xi_p} \simeq 1 + \frac{N}{\xi_p} + \frac{1}{2}\frac{N^2}{\xi_p^2} = 1 + N \ln c + \frac{1}{2} N^2 (\ln c)^2$$

When is it that $N|\ln c| < 1$? When $|\ln c| \simeq 0$

$\Rightarrow$ $c \sim 1$ $\Rightarrow$ $\langle \cos\theta \rangle \sim 1$ $\Rightarrow$ very stiff!

$$c = 1 - \varepsilon \quad \Rightarrow \quad \ln c = \ln(1-\varepsilon) \simeq -\varepsilon - \frac{1}{2}\varepsilon^2 - \frac{1}{3}\varepsilon^2$$

Thus

$$c^N \simeq 1 - N\left(\varepsilon + \tfrac{1}{2}\varepsilon^2\right) + \tfrac{1}{2}N^2(\ln c)^2$$

We finally rewrite everything

$$\frac{1}{b^2}\langle \vec{R}_{ee}^{\,2} \rangle = \frac{1+c}{1-c}N + 2\frac{c}{1-c} - 2c\frac{c-c^N}{(1-c)^2} =$$

$$= \frac{1+c}{1-c}N + 2\frac{c}{1-c}\left(1 - \frac{c}{1-c}\right) + 2\frac{c}{1-c}c^N =$$

$$= \frac{1+c}{1-c}N + 2\frac{c(1-2c)}{(1-c)^2} + 2\frac{c}{1-c}c^N =$$

$$= \frac{1}{1-c}\left[(1+c)N + \frac{2c}{1-c}c^N\right] + 2\frac{c(1-2c)}{(1-c)^2}$$

We then write $c^N = e^{N\ln c} \simeq 1 + N\ln c + \frac{1}{2}N^2(\ln c)^2$

$$\Rightarrow \quad (1+c)N + \frac{2c}{1-c}c^N \simeq (1+c)N + \frac{2c}{1-c} + \frac{2c}{1-c}\ln c\, N + N^2\frac{c(\ln c)^2}{1-c}$$

We first focus on the term which is linear in N:

$$1 + c + \frac{2c}{1-c}\ln c \underset{c=1-\varepsilon}{\simeq} 2 - \varepsilon + \frac{2(1-\varepsilon)\left(-\varepsilon - \frac{1}{2}\varepsilon^2\right)}{\varepsilon} =$$

$$= 2 - \varepsilon - 2(1-\varepsilon)\left(1 + \tfrac{1}{2}\varepsilon\right) = 2 - \varepsilon - 2\left(1 - \varepsilon + \tfrac{1}{2}\varepsilon - \tfrac{1}{2}\varepsilon^2\right) = \varepsilon^2$$

And plugging it back in $\frac{1}{b^2}\langle \vec{R}_{ee}^{\,2}\rangle$, always with $c = 1-\varepsilon$, we have

$$\frac{1}{b^2}\langle \vec{R}_{ee}^{\,2}\rangle \simeq \frac{1}{\varepsilon}\left[\varepsilon^2 N + \frac{c(\ln c)^2}{1-c}N^2 + \frac{2c}{1-c}\right] - 2\,\frac{c}{(1-c)^2} =$$

$$= \varepsilon N + \frac{1}{\varepsilon}\,\frac{(1-\varepsilon)\,\varepsilon^2}{\varepsilon}N^2 + \frac{2(1-\varepsilon)}{\varepsilon^2} - \frac{2(1-\varepsilon)}{\varepsilon^2}$$

$$\simeq (1-\varepsilon)N^2 + \varepsilon N$$

Also, recall that $\xi_p = \frac{1}{|\ln c|} = \frac{1}{|\ln(1-\varepsilon)|} \simeq \frac{1}{\varepsilon}$, so if $\varepsilon \to 0$ then $\xi_p \to \infty$ and we can rewrite

$$\frac{1}{b^2}\langle \vec{R}_{ee}^{\,2}\rangle \simeq N^2 + \frac{N}{\xi_p}$$

We find an expected result: if the polymer is very rigid, then we expect its end-to-end distance to be proportional to the number of segments:

$$\frac{1}{b^2}\langle \vec{R}_{ee}^{\,2}\rangle \sim N^2$$

This is true if the linear term vanishes: $N \ll \xi_p$

Introducing back the length of the vectors, b:

$$\langle \vec{R}_{ee}^{\,2}\rangle \simeq b^2N^2 + \frac{b^2 N}{\xi_p} = b^2N^2 + b^2\frac{bN}{b\xi_p} = L^2 + b^2\left(\frac{L}{\ell_p}\right)$$

where we recall that $L = bN$ is the length of the polymer and ℓ_p is the persistence length.

We have in the end the following result for the KP model :

$$\langle \vec{R}_{ee}^{\,2} \rangle \simeq \begin{cases} b^2N^2 & L \ll \ell_p \\ b^2N & L \gg \ell_p \end{cases}$$

$c = 1-\varepsilon$ and ε small

furthermore, the Kuhn length $\ell_K = \frac{1+c}{1-c}\, b \overset{\downarrow}{\simeq} \frac{2}{\varepsilon}\, b \simeq 2\ell_p$

Lexicon : a polymer described by the KP model is also called a "semi-flexible" polymer.

2) What about 3D ?

the calculation of $\vec{r}_i \cdot \vec{r}_j$ in two dimensions was easy because it reduced to

$$\vec{r}_i \cdot \vec{r}_j = b^2 \cos\left(\sum_{l=i}^{j-1} \theta_l \right)$$

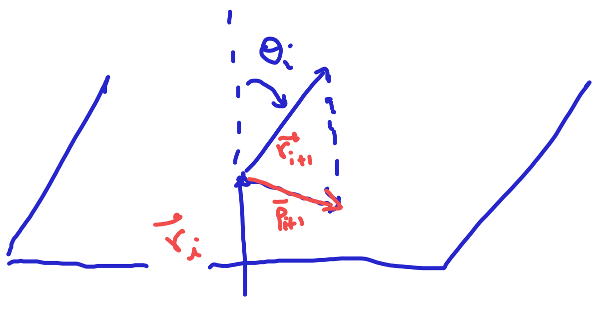
without the need to take into account any other angle.

This is clearly not the case in higher dimensions.

How do we deal with higher dimensions, then ?

Let's work out 2 simple cases and then we generalise :

1) $\langle \vec{r}_{i+1} \cdot \vec{r}_i \rangle$:



a plane in 3D

we call $\vec{P}_{i+1}$ the projection of $\vec{r}_{i+1}$ on the space orthogonal to $\vec{r}_i$.

Then we can write :

$$\vec{r}_{i+1} = \cos\theta_i \, \vec{r}_i + \vec{P}_{i+1}$$

then we have

$$\vec{r}_{i+1}\cdot\vec{r}_i = \cos\theta_i \underbrace{\vec{r}_i\cdot\vec{r}_i}_{=b^2} + \overbrace{\vec{\rho}_{i+1}\cdot\vec{r}_i}^{=0}$$

because $\vec{\rho}_{i+1} \perp \vec{r}_i$ by construction

and finally

$$\langle \vec{r}_{i+1}\cdot\vec{r}_i \rangle = b^2 \langle \cos\theta_i \rangle$$

2) $\langle \vec{r}_{i+2}\cdot\vec{r}_i \rangle$

We can repeat exactly the same procedure as before, expressing $\vec{r}_{i+2}$ by means of $\vec{r}_{i+1}$:

$$\vec{r}_{i+2} = \cos\theta_{i+1}\,\vec{r}_{i+1} + \vec{\rho}_{i+2}$$

so that

$$\vec{r}_{i+2}\cdot\vec{r}_i = \cos\theta_{i+1}\,\vec{r}_{i+1}\cdot\vec{r}_i + \vec{\rho}_{i+2}\cdot\vec{r}_i =$$

$$= \cos\theta_{i+1}\left(\cos\theta_i\,\vec{r}_i + \vec{\rho}_{i+1}\right)\cdot\vec{r}_i + \vec{\rho}_{i+2}\cdot\vec{r}_i =$$

$$= b^2\cos(\theta_{i+1})\cos(\theta_i) + \vec{\rho}_{i+2}\cdot\vec{r}_i$$

Then we take the average

$$\langle \vec{r}_{i+2}\cdot\vec{r}_i \rangle = b^2 \underbrace{\langle \cos\theta_{i+1} \rangle \langle \cos\theta_i \rangle} + \underbrace{\langle \vec{\rho}_{i+2} \rangle \cdot \langle \vec{r}_i \rangle}$$

recall that we are assuming that angles are independent

again we factorize because $\vec{\rho}_{i+2}$ only depends on the angles between $\vec{r}_{i+1}$ and $\vec{r}_{i+2}$ but not $\vec{r}_i$, and the angles for different vector pairs are indep.

If $u(\theta_i)$ is invariant for rotations around $\vec{r}_i$ (and similarly for $\forall i$) then $\langle \vec{\rho}_{i+2} \rangle = 0$ by isotropy

We can extend the reasoning to any further pair, finding

$$\langle \vec{r}_j \cdot \vec{r}_i \rangle = b^2 \left\langle \prod_{l=i}^{j-1} \cos\theta_l \right\rangle = b^2 c^{j-i} \qquad (j>i)$$

as before.

3) Continuum limit

The discrete step representation is convenient for some types of calculations (e.g. simulations) but is not necessarily the best for others. It is always useful to have alternate approaches, and the continuum one is typical in physics, because it captures what we observe when we "zoom out" from the system (think about a block of metal: microscopically it is made of atoms, at large enough scales we use continuum mechanics).

In this case we have that the polymer is made of N vectors of length b, we would have 2N vectors of length $b/2$, and, more generally:

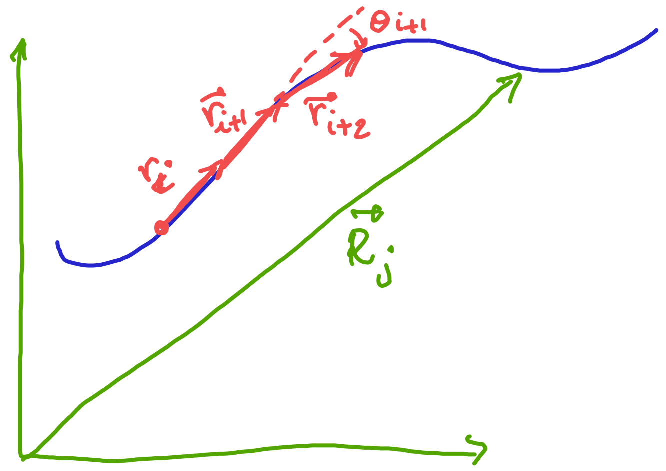
$$b \to 0 \qquad N \to \infty \qquad \text{while} \qquad \underline{b \cdot N = L} \quad \text{fixed}$$

also, we know that

$l_p = b\,\xi_p = b\dfrac{1}{|\ln c|}$ which is an intrinsic property of the polymer

We must now obtain the energy of the system :

$$E(\{\theta_i\}) = -\varepsilon\sum_i \cos\theta_i = -\frac{\varepsilon}{b^2}\sum_i \vec{r}_i\cdot\vec{r}_{i+1}$$



Then

$$\vec{r}_{i+1}\cdot\vec{r}_i = -\frac{1}{2}\left(\vec{r}_{i+1}-\vec{r}_i\right)\cdot\left(\vec{r}_{i+1}-\vec{r}_i\right)+b^2$$

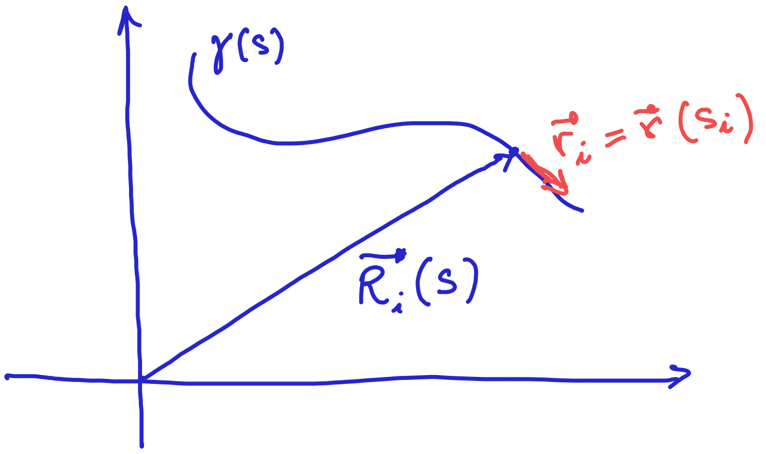
$$\Downarrow$$

$$E(\{\theta_i\}) = \frac{\varepsilon}{2b^2}\sum_i\left(\vec{r}_{i+1}-\vec{r}_i\right)\cdot\left(\vec{r}_{i+1}-\vec{r}_i\right)\underbrace{-\varepsilon N}_{\text{can be neglected because it is a constant}}$$

Then we have

$$E(\{\theta_i\}) = \frac{\varepsilon}{2b^2}\sum_i\left(\vec{r}_{i+1}-\vec{r}_i\right)\cdot\left(\vec{r}_{i+1}-\vec{r}_i\right)$$

For a continuous curve, with curve parameter s, $\vec{r}_i$ is the tangent vector to the curve in s_i



$$\Rightarrow \vec{r}_i \approx \frac{\partial \vec{R}_i}{\partial s}$$

and we know that

$$\sum_{i=1}^{N}|\vec{r}_i| = \nearrow \sum_{i=1}^{N} b = Nb = L$$

$$\searrow \sum_{i=1}^{N}|\vec{r}(s_i)|\overbrace{\Delta i}^{=1} =$$

$$= \sum_{i=1}^{N}\underbrace{|\hat{E}(s_i)|}_{=1}\underbrace{b\Delta i}_{\substack{\to 0\\ \text{if } b\to 0}} = \int_0^L ds = L$$

Which means that

$$E(\gamma) = \frac{\varepsilon}{2b^2} \sum_{i=1}^{N} (\vec{r}_{i+1} - \vec{r}_i)\cdot(\vec{r}_{i+1} - \vec{r}_i) =$$

$$= \frac{\varepsilon}{2} \sum_{i=1}^{N} (\hat{t}_{i+1} - \hat{t}_i)(\hat{t}_{i+1} - \hat{t}_i) \overbrace{\Delta i}^{1} =$$

$$= \frac{\varepsilon}{2} b \sum_{i=1}^{N} \left(\frac{\hat{t}_{i+1} - \hat{t}_i}{b}\right)\cdot\left(\frac{\hat{t}_{i+1} - \hat{t}_i}{b}\right)(b\Delta i) \underset{\overset{\uparrow}{b \to 0}}{=} \frac{\varepsilon b}{2} \int_0^L \left(\frac{\partial \hat{t}}{\partial s}\right)^2 ds$$

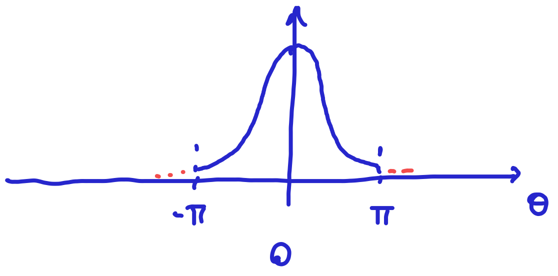
We must then connect ε to the persistence length ℓ_p. To do so, we assume, reasonably, that the polymer on small scales is rigid (ε large) so that only the region close to the minimum of the potential matters (small thermal fluctuations). In this limit, we can expand the potential (here we focus on a single angle!)

$$E(\theta) = -\varepsilon \cos\theta \simeq \frac{1}{2} \varepsilon \theta^2$$

and we have thus (in 2D for simplicity):

$$C = \langle \cos\theta \rangle = \frac{\int_{-\pi}^{\pi} \cos\theta \; e^{-\frac{1}{2}\frac{\varepsilon}{k_BT}\theta^2} d\theta}{\int_{-\pi}^{\pi} e^{-\frac{1}{2}\frac{\varepsilon}{k_BT}\theta^2} d\theta}$$

But



$$\Rightarrow \int_{-\pi}^{\pi} e^{-\frac{1}{2}\frac{\varepsilon}{k_BT}\theta^2} d\theta \simeq \int_{-\infty}^{+\infty} e^{-\frac{1}{2}\frac{\varepsilon}{k_BT}\theta^2} d\theta =$$

$$= \sqrt{\frac{2\pi k_BT}{\varepsilon}}$$

So that

$$\underline{c} = \sqrt{\frac{\varepsilon}{2\pi k_B T}} \int_{-\infty}^{+\infty} \cos\theta \; e^{-\frac{1}{2}\frac{\varepsilon}{k_B T}\theta^2} \, d\theta =$$

$$\simeq \sqrt{\frac{\varepsilon}{2\pi k_B T}} \int_{-\infty}^{+\infty} \left(1 - \frac{1}{2}\theta^2\right) e^{-\frac{1}{2}\frac{\varepsilon}{k_B T}\theta^2} \, d\theta = \underline{1 - \frac{1}{2}\frac{k_B T}{\varepsilon}}$$

We now use

$$\ell_p = b\,\xi_p = b \frac{1}{|\ln c|} \simeq b \frac{1}{\frac{1}{2}\frac{k_B T}{\varepsilon}} = \frac{2 b \varepsilon}{k_B T}$$

So that, as in some reference literature, we could write

$$b\,\varepsilon = \frac{k_B T \,\ell_p}{2}$$

$$\Downarrow$$

$$E(\gamma) = \frac{1}{2} \frac{k_B T\, \ell_p}{2} \int_0^L \left(\frac{\partial \hat{t}}{\partial s}\right)^2 ds$$

What is nice here is that the prefactor depends only on

1) ε and b $\Rightarrow$ length of a monomer and bending energy between monomers

2) T and ℓ_p $\Rightarrow$ Both measurable

$\rightarrow$ both objective quantities that do not depend on the representation.

But $c \to 1$ means (here for simplicity in 2D):

$$c = \langle \cos\theta \rangle = \frac{\int_0^{2\pi} d\theta \, \cos\theta \, e^{-\beta u(\theta)}}{\int_0^{2\pi} d\theta \, e^{-\beta u(\theta)}} \longrightarrow 1$$

$\cos\theta \simeq 1$ only close to $\theta \simeq 0$, which implies that

$$p(\theta) = \frac{e^{-\beta u(\theta)}}{\int_0^{2\pi} d\theta \, e^{-\beta u(\theta)}}$$

must be peaked around $\theta = 0$, and progressively so

Furthermore we have that $u(\theta) = u(-\theta)$ and we can approximate $u(\theta)$ as $u(\theta) \simeq \frac{1}{2}\frac{\theta^2}{a_N}$, and

$$p(\theta) = \frac{1}{\sqrt{2\pi a_N k_B T}} \, e^{-\frac{1}{2}\frac{\beta\theta^2}{a_N}}$$

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

If a_N is small enough for large N:

$$\langle \cos\theta \rangle \simeq \frac{1}{\sqrt{2\pi a_N k_B T}} \int_0^{2\pi} \cos\theta \, e^{-\frac{\beta}{2a_N}\theta^2} d\theta \simeq \frac{1}{\sqrt{2\pi a_N k_B T}} \int_0^{2\pi} \left(1 - \tfrac{1}{2}\theta^2\right) e^{-\frac{\beta}{2a_N}\theta^2} d\theta =$$

$$= 1 - \frac{1}{2}\langle \theta^2 \rangle = 1 - \frac{1}{2}\frac{a_N}{\beta} = 1 - \frac{k_B T}{2} a_N$$

Recalling that

$$\frac{\ell_p}{L} = \frac{1}{N|\ln c|} = \frac{1}{N\left|\ln\left(1 - \frac{k_B T}{2} a_N\right)\right|} \simeq \frac{1}{N \frac{k_B T}{2} a_N}$$

$$\Rightarrow \quad a_N = \frac{2L}{\ell_p k_B T} \frac{1}{N}$$

and finally

$$P_\Theta = \frac{1}{\sqrt{2\pi \frac{2L}{k_B T} \frac{1}{N}}} \, e^{-\frac{1}{2} \frac{l_p}{2L} N \Theta^2}$$