Part I
Statistical Mechanics of Biopolymers

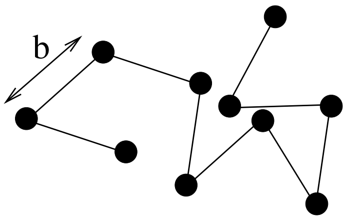
1 Random walk models for the conformation

In this chapter we study statistical models for polymers which have in common that the polymer is considered as a chain of rigid links which are oriented randomly.

1.1 The freely jointed chain

We consider a chain consisting of segments which all have the length b. This is not necessarily a monomer length, depending on the polymer type it can be 4 or 5 monomers long.

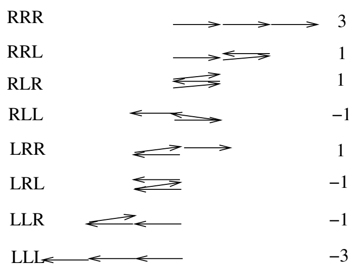
Figure 1: freely jointed chain model



1.1.1 Random walk in one dimension

Let us start with the simple model of a 1-dimensional chain. For example consider the possible configurations of a chain with only three segments:

Figure 2: configurations of a 1-dimensional chain



A chain with M segments has a total of 2^M different configurations which will be denoted by the sequence of distance vectors.

$$(b_1, b_2, \cdots b_N) \quad b_j = \pm b$$

If the random walk choses with equal probability of $\frac{1}{2}$ steps to the left or right side, every configuration appears with a probability of

$$P(b_1, b_2, \cdots b_N) = 2^{-M}$$

Now consider the end-to-end distance

$$L = \sum_{j=1}^{M} b_j$$

The probability to find a certain value of L can be determined from the binomial distribution

$$(\frac{1}{2} + \frac{1}{2})^M = \sum_{M_r=0}^{M} \frac{1}{2}^{M_r} \frac{1}{2}^{M-M_r} \frac{M!}{M_r!(M-M_r)!}$$

as

$$P(L = M_r b + (M - M_r)(-b)) = P(L = (2M_r - M)b) = 2^{-M} \frac{M!}{M_r!(M-M_r)!}$$

or

$$P(L) = 2^{-M} \frac{M!}{\left(\frac{\frac{L}{b}+M}{2}\right)! \left(\frac{M-\frac{L}{b}}{2}\right)!}$$

where $\frac{L}{b}$ has to be an even integer for M even and an odd integer for odd M.

The maximum of this distribution is at $M_r = \frac{M}{2}$ for even M and at $M_r = \frac{M\pm1}{2}$ for odd M. This can be easily seen for even M from

$$(\frac{M}{2} - 1)!(M - \frac{M}{2} + 1)! = (\frac{M}{2} + 1)!(M - \frac{M}{2} - 1)! =$$

$$= \left(\frac{M}{2} + 1\right)! \left(\frac{M}{2} - 1\right)! = 1 \cdot 2 \cdot \cdots (\frac{M}{2})(\frac{M}{2} + 1) \cdot 1 \cdot 2 \cdots (\frac{M}{2} - 2)(\frac{M}{2} - 1)$$

$$= (\frac{M}{2})!(\frac{M}{2} + 1)(\frac{M}{2})!(\frac{M}{2})^{-1} = (\frac{M}{2})!(M - \frac{M}{2})! \frac{M+2}{M} > (\frac{M}{2})!(M - \frac{M}{2})!$$

and for odd M from

$$(\frac{M-1}{2} - 1)!(M - \frac{M-1}{2} + 1)! = (\frac{M+1}{2} + 1)!(M - \frac{M+1}{2} - 1)! = (\frac{M+3}{2})!(\frac{M-3}{2})! =$$

$$1 \cdot 2 \cdots \frac{M+1}{2} \cdot \frac{M+3}{2} \cdot 1 \cdot 2 \cdots \frac{M-3}{2} = (\frac{M+1}{2})! \frac{M+3}{2} (\frac{M-1}{2})! (\frac{M-1}{2})^{-1}$$

$$= (\frac{M-1}{2})!(M - \frac{M-1}{2})! \frac{M+3}{M-1} > (\frac{M-1}{2})!(M - \frac{M-1}{2})!$$

Let us calculate the first two moments of the distribution of lengths

$$\overline{M_r} = \sum_{M_r=0}^{M} p^{M_r} q^{M-M_r} M_r \frac{M!}{M_r!(M-M_r)!} = p\frac{\partial}{\partial p} \sum_{M_r=0}^{M} p^{M_r} q^{M-M_r} \frac{M!}{M_r!(M-M_r)!} = p\frac{\partial}{\partial p}(p+q)^M$$

$$= pM(p+q)^{M-1} = \frac{M}{2}$$

and hence

$$\overline{L} = (2\overline{M_r} - M)b = 0$$

The second moment follows from

$$\overline{M_r^2} = \sum_{M_r=0}^{M} p^{M_r} q^{M-M_r} M_r^2 \frac{M!}{M!(M-M_r)!} = (p\frac{\partial}{\partial p})(p\frac{\partial}{\partial p}) \sum_{M_r=0}^{M} p^{M_r} q^{M-M_r} \frac{M!}{M_r!(M-M_r)!}$$

$$= (p\frac{\partial}{\partial p})(pM(p+q)^{M-1}) = pM((p+q)^{M-1} + p^2 M(M-1)(p+q)^{M-2})$$

$$\frac{M}{2} + \frac{M(M-1)}{4}) = \frac{M^2}{4} + \frac{M}{4}$$

and the standard deviation is given by

$$(\Delta M)^2 = \overline{M_r^2} - \overline{M_r}^2 = \frac{M}{4}$$

example for $M = 1000$ the standard deviation is $\Delta M \approx 16$ and the relative uncertainty $\Delta M/\overline{M} = 1/\sqrt{M} \approx 3\%$

For the end-to end length we have

$$\overline{L^2} = b^2 \overline{(2M_r - M)^2} = b^2(4\overline{M_r^2} - 4M\overline{M_r} + M^2) = b^2(M^2 + M - 2M^2 + M^2) = Mb^2$$

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1.1.2 Entropic elasticity

We consider L as a macroscopic variable. The number of configurations with length L is given by

$$\Omega(L) = \frac{M!}{\left(\frac{\frac{L}{b}+M}{2}\right)! \left(\frac{M-\frac{L}{b}}{2}\right)!}$$

The free energy is (no internal degrees of freedom, $E = 0$)

$$F = -TS = -kT \ln \Omega$$

which using Stirling's approximation for large number M gives

$$F = -kTM \ln M + kT\frac{M + \frac{L}{b}}{2} \ln \frac{M + \frac{L}{b}}{2} + kT\frac{M - \frac{L}{b}}{2} \ln \frac{M - \frac{L}{b}}{2}$$

$$= -MkT\ln 2 - MkT\ln M + \frac{M}{2}kT\ln(M^2 - \frac{L}{b^2}^2) + \frac{L}{2b}kT\ln\frac{Mb+L}{Mb-L}$$

If the system is close to its most probable state ($L = 0$) we can apply a Taylor series expansion to have

$$F = -MkT\ln 2 + kT\frac{1}{2Mb^2}L^2 + \cdots$$

The quadratic dependence on L is very similar to a Hookean spring. For a potential energy

$$V = \frac{k_s}{2}x^2$$

the probability distribution of the coordinate is

$$P(x) = \sqrt{\frac{k_s}{2\pi k_b T}}e^{-k_s x^2/2k_b T}$$

which gives a free energy of

$$F = -kT\ln P = \text{const} + \frac{k_s x^2}{2}$$

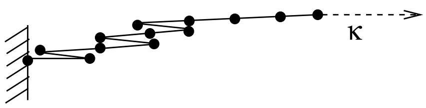
From comparison the apparent spring constant is

$$k_s = \frac{kT}{Mb^2}$$

1.1.3 force extension relationship

Consider now an external force κ trying to stretch the polymer

Figure 3: external force acting on the polymer



The differential of the free energy is now given by

$$dF = -SdT + \kappa dL$$

from which we find (an Algebra program is very helpful here)

$$\kappa = \frac{\partial F}{\partial L}|_T = \frac{kT}{2b}\ln\left(\frac{Mb+L}{Mb-L}\right)$$

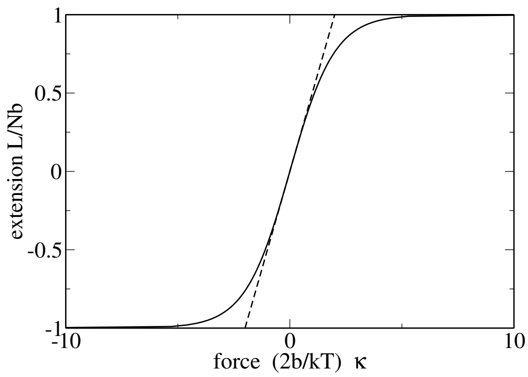
For a highly stretched polymer the maximum value of $L_{max} = Mb$ cannot be exceeded. Close to the equilibrium we have the linear relationship

$$\kappa = \frac{\partial F}{\partial L}|_T = \frac{kT}{Mb^2}L$$

and the length as a function of the force is

$$L = \frac{Mb^2}{kT}\kappa$$

Figure 4: force-extension relation



1.1.4 3-dimensional freely jointed chain

We consider now a 3-dimensional chain consisting of M units. The configuration can be described by a point in a 3(M+1)-dimensional space

$$(\vec{r}_0, \vec{r}_2 \cdots \vec{r}_M)$$

The M bond vectors

$$\vec{b}_i = \vec{r}_i - \vec{r}_{i-1}$$

have a fixed length $|\vec{b}_i| = b$ and are oriented randomly. This can be described by a distribution function

$$P(\vec{b}_i) = \frac{1}{4\pi b^2}\delta(|b_i| - b)$$

Since the different units are independent the joint probability distribution factorizes

$$P(\vec{b}_1 \cdots \vec{b}_M) = \prod_{i=1}^{M} P(\vec{b_i})$$

There is no excluded volume interaction between any two monomers. Obviously the end to end distance

$$\vec{R} = \sum_{i=1}^{N} \vec{b}_i$$

has an average value of $\overline{\vec{R}} = 0$ since

$$\overline{\vec{R}} = \sum \overline{\vec{b}_i} = M \int \vec{b}_i P(\vec{b}_i) = 0$$

The second moment is

$$\overline{R^2} = \overline{\left(\sum_i \vec{b}_i \sum_j \vec{b}_j \right)} = \sum_{i,j} \overline{\vec{b}_i \vec{b}_j}$$

$$= \sum_i \overline{b_i^2} + \sum_{i \neq j} \overline{\vec{b}_i \vec{b}_j} = Mb^2$$

The distribution of the end to end vector is

$$P(\vec{R}) = \int P(\vec{b}_1 \cdots \vec{b}_M) \delta \left(\vec{R} - \sum \vec{b}_i \right) d^3 b_1 \cdots d^3 b_M$$

This integral can be evaluated by replacing the delta function by the Fourier integral

$$\delta(\vec{R}) = \frac{1}{(2\pi)^3} \int e^{-i\vec{k}\vec{R}} d^3 k$$

which gives

$$P(\vec{R}) = \int d^3 k e^{-i\vec{k}\vec{R}} \prod_{i=1}^{M} \left(\int \frac{1}{4\pi b^2} \delta(|\vec{b}_i| - b) e^{i\vec{k}\vec{b}_i} d^3 b_i \right)$$

The inner integral can be evaluated in polar coordinates

$$\int \frac{1}{4\pi b^2} \delta(|\vec{b}_i| - b) e^{i\vec{k}\vec{b}_i} d^3 b_i =$$

$$= \int_0^{2\pi} d\phi \int_0^{\infty} b_i^2 db_i \frac{1}{4\pi b^2} \delta(|b_i| - b) \int_0^{\pi} \sin\theta d\theta e^{ikb_i \cos\theta}$$

The integral over θ gives

$$\int_0^{\pi} \sin\theta d\theta e^{ikb_i \cos\theta} = \frac{2 \sin kb_i}{kb_i}$$

and hence

$$\int \frac{1}{4\pi b^2} \delta(|\vec{b}_i| - b) e^{i\vec{k}\vec{b}_i} d^3 b_i = 2\pi \int_0^{\infty} db_i \frac{1}{4\pi b^2} \delta(b_i - b) b_i^2 \frac{2 \sin kb_i}{kb_i}$$

$$= \frac{\sin kb}{kb}$$

and finally we have

$$P(\vec{R}) = \frac{1}{(2\pi)^3} \int d^3 k e^{-i\vec{k}\vec{R}} \left(\frac{\sin kb}{kb} \right)^M$$

The function

$$\left(\frac{\sin kb}{kb} \right)^M$$

has a very sharp maximum at $kb = 0$. For large M it can be approximated quite accurately by a Gaussian

$$\left(\frac{\sin kb}{kb} \right)^M \approx e^{-M \frac{1}{6} k^2 b^2}$$

which gives

$$P(\vec{R}) \approx \frac{1}{(2\pi)^3} \int d^3k e^{-i\vec{k}\vec{R}} e^{-\frac{M}{6}k^2b^2}$$
$$= \left(\frac{3}{2\pi b^2 M}\right)^{3/2} e^{-3R^2/(2b^2M)}$$

similar to the 1-dimensional case. The apparent spring constant follows from the comparison

$$e^{-\frac{k_s}{2}R^2/kT} = e^{-3R^2/(2b^2M)}$$

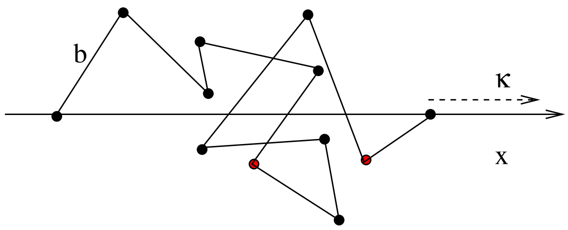
and is

$$k_s = \frac{3kT}{Mb^2}$$

1.1.5 force-extension relation for the 3-d chain

We consider now a 3-dimensional chain with one fixed end and an external force acting in x-direction at the other end.

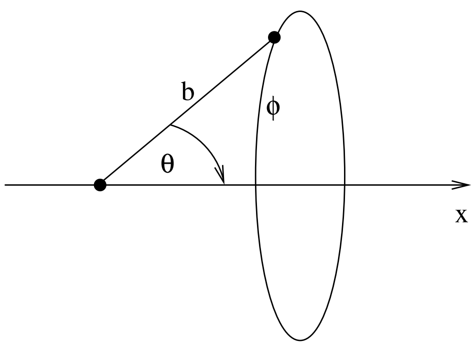
Figure 5: 3-d chain with external force



The projection of the i-th segment onto the x-axis has a length of

$$b_j = -b\cos\theta \in [-b, b]$$

Figure 6: projection of the bond vector



We discretize the continuous range of b_j by dividing the interval $[-b, b]$into n bins of width $\Delta b = \frac{2b}{n}$ corresponding to the discrete values l_i $i = 1 \cdots n$. The chain members are divided into n groups according to their bond projections b_j. The number of units in each group is denoted by M_i so that

$$\sum_{i=1}^{n} M_i = M$$

and the end to end length is

$$\sum_{i=1}^{n} l_i M_i = L$$

The probability distribution is

$$P(\theta, \phi) d\theta d\phi = \frac{\sin(\theta) d\theta d\phi}{4\pi}$$

Since we are only interested in the probability of the l_i , we integrate over ϕ

$$P(\theta) d\theta = \frac{\sin(\theta) d\theta}{2}$$

and transform variables to have

$$P(l) dl = P(-b\cos\theta) d(-b\cos\theta) = \frac{1}{2b} d(-b\cos\theta) = \frac{1}{2b} dl$$

The canonical partition function is

$$Z(L, M, T) = \sum_{\{M_i\} \sum M_i l_i = L} \frac{M!}{\prod_j M_j!} \prod_i z_i^{M_i} = \sum_{\{M_i\}} M! \prod_i \frac{z_i^{M_i}}{M_i!}$$

The $z_i = z$ are the independent partition functions of the single units which we assume as independent of i. The degeneracy factor $\frac{M!}{\prod M_i!}$counts the number of microstates for a certain configuration $\{M_i\}$. The summation is only over configurations with a fixed end to end length. This makes the evaluation rather complicated. Instead we introduce a new partition function by considering an ensemble with fixed force and fluctuating length

$$\Delta(\kappa, M, T) = \sum_L Z(L, M, T) e^{\frac{\kappa L}{kT}}$$

Approximating the logarithm of the sum by the logarithm of the maximum term we see that

$$-kT \ln \Delta = -kT \ln Z - \kappa L$$

($-\kappa L$ corresponds to $+pV$) gives the (Gibbs) free enthalpy

$$G(\kappa, M, T) = F - \kappa L$$

In this new ensemble the summation over L simplifies the partition function

$$\Delta = \sum_{\{M_i\}} e^{\frac{\kappa \sum M_i l_i}{kT}} M! \prod \frac{z^{M_i}}{M_i!} = \sum_{\{M_i\}} M! \prod \frac{(z e^{\frac{\kappa l_i}{kT}})^{M_i}}{M_i!}$$

$$= \left(\sum z e^{\frac{\kappa l_i}{kT}}\right)^M$$

$$= \xi(\kappa, T)^M$$

Now returning to a continuous distribution of $l_i = -b\cos\theta$ we have to evaluate

$$\xi = \int_{-b}^{b} P(l)dl \quad z e^{\frac{l\kappa}{kT}} = z\frac{\sinh t}{t}$$

with

$$t = \frac{\kappa b}{kT}$$

From

$$dG = -SdT - Ld\kappa$$

we find

$$L = -\frac{\partial G}{\partial \kappa}|_T$$

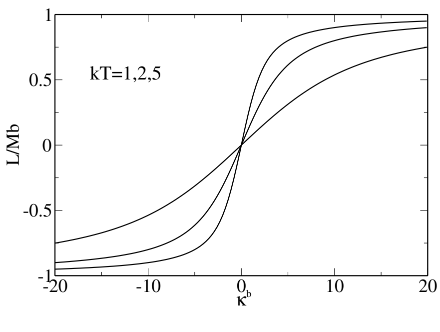
$$= \frac{\partial}{\partial \kappa}\left(MkT\ln\left(\frac{z}{\frac{\kappa b}{kT}}\sinh\frac{\kappa b}{kT}\right)\right)$$

$$= MkT\left(-\frac{1}{\kappa} + \frac{b}{kT}\coth\left(\frac{\kappa b}{kT}\right)\right) = Mb\mathfrak{L}\left(\frac{\kappa b}{kT}\right)$$

with the Langevin function

$$\mathfrak{L}(x) = \coth(x) - \frac{1}{x}$$

Figure 7: Force - extension relation for the 3-dim chain

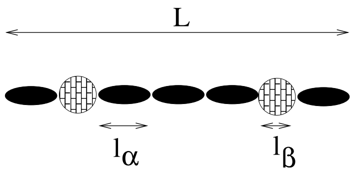


1.2 two component model

The 1-dimensional random walk model can be also applied to a polymer chain which is composed of two types of units (named α and β) , which may interconvert. An example would be DNA, which may be in α-configuration and Z-configuration, respectively.

We assume that of the overall M units M_α are in the α-configuration and $M - M_\alpha$ are in the β-configuration. The lengths of the two conformers are l_α and l_β , respectively.

Figure 8: two component model



The total length is given by

$$L = M_\alpha l_\alpha + (M - M_\alpha) l_\beta = M_\alpha (l_\alpha - l_\beta) + M l_\beta$$

The number of configurations with length L is given by

$$\Omega(L) = \Omega(M_\alpha = \frac{L - M l_\beta}{l_\alpha - l_\beta}) = \frac{M!}{\left(\frac{L - M l_\beta}{l_\alpha - l_\beta}\right)! \left(\frac{M l_\alpha - L}{l_\alpha - l_\beta}\right)!}$$

From the partition function

$$Z = z_\alpha^{M_\alpha} z_\beta^{M - M_\alpha} \Omega = z_\alpha^{\frac{L - M l_\beta}{l_\alpha - l_\beta}} z_\beta^{\frac{M l_\alpha - L}{l_\alpha - l_\beta}} \Omega$$

application of Stirling's approximation gives for the free energy

$$F = -kT \ln Z =$$

$$= -kT \frac{L - M l_\beta}{l_\alpha - l_\beta} \ln z_\alpha - kT \frac{M l_\alpha - L}{l_\alpha - l_\beta} \ln z_\beta - kT \left(M \ln M - M\right)$$

$$-kT \left\{ -\left(\frac{L - M l_\beta}{l_\alpha - l_\beta}\right) \ln \left(\frac{L - M l_\beta}{l_\alpha - l_\beta}\right) + \left(\frac{L - M l_\beta}{l_\alpha - l_\beta}\right) - \left(\frac{M l_\alpha - L}{l_\alpha - l_\beta}\right) \ln \left(\frac{M l_\alpha - L}{l_\alpha - l_\beta}\right) + \left(\frac{M l_\alpha - L}{l_\alpha - l_\beta}\right) \right\}$$

The derivative of the free energy gives the force extension relation

$$\kappa = \frac{\partial F}{\partial L} = \frac{kT}{l_\alpha - l_\beta} \ln \left(\frac{M l_\beta - L}{L - M l_\alpha}\right) + \frac{kT}{l_\alpha - l_\beta} \ln \frac{z_\beta}{z_\alpha}$$

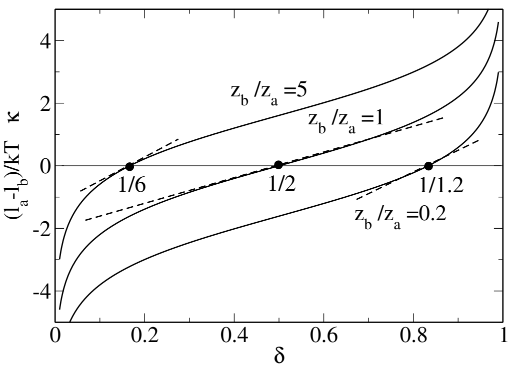
this can be written as a function of the fraction of segments in the α-configuration

$$\delta = \frac{M_\alpha}{M} = \frac{L - Ml_\beta}{M(l_\alpha - l_\beta)}$$

in the somewhat simpler form

$$\kappa \frac{l_\alpha - l_\beta}{kT} = \ln \frac{\delta}{1-\delta} + \ln \frac{z_\beta}{z_\alpha}$$

Figure 9: force-extension relation for the 2-component model



The mean extension for zero force is obtained by solving $\kappa(L) = 0$

$$\overline{L}_0 = M\left(\frac{z_\alpha l_\alpha + z_\beta l_\beta}{z_\alpha + z_\beta}\right)$$

$$\delta_0 = \frac{\bar{L}_0 - Ml_\beta}{M(l_\alpha - l_\beta)} = \frac{z_\alpha}{z_\alpha + z_\beta}$$

Taylor series expansion around $\overline{L}_0$ gives the linearized force-extension relation

$$\kappa = \frac{\partial F}{\partial L} = \frac{kT}{M(l_\alpha - l_\beta)^2}\frac{(z_\alpha + z_\beta)^2}{z_\alpha z_\beta}(L - \bar{L}_0) + \cdots = \frac{kT}{l_\alpha - l_\beta}\frac{(z_\alpha + z_\beta)^2}{z_\alpha z_\beta}(\delta - \delta_0)$$

1.3 two component model with interactions

We consider now additional interaction between neighbouring units. We introduce the interaction energies $w_{\alpha\alpha}, w_{\alpha\beta}, w_{\beta\beta}$ for the different pairs of neighbours and the numbers $N_{\alpha\alpha}, N_{\alpha,\beta}, N_{\beta\beta}$ of such interaction terms. The total interaction energy is then

$$W = N_{\alpha\alpha} w_{\alpha\alpha} + N_{\alpha\beta} w_{\alpha\beta} + N_{\beta\beta} w_{\beta\beta}$$

The numbers of pair interactions are not independent from the numbers of units M_α, M_β. Consider insertion of an additional α-segment into a chain. The following figure counts the possible changes in interaction terms. In any case by insertion of an α-segments the expression $2N_{\alpha\alpha} + N_{\alpha\beta}$ increases by 2.

Figure 10: insertion of an α-segment

α ↓	M_α	M_β	$N_{\alpha\alpha}$	$N_{\alpha\beta}$	$N_{\beta\beta}$	$2N_{\alpha\alpha}+N_{\alpha\beta}$
αα	+1		+1			+2
αβ	+1		+1			+2
βα	+1		+1			+2
ββ	+1			+2	−1	+2

Similarly, insertion of an extra β-segment increases $2N_{\beta\beta} + N_{\alpha\beta}$ by 2.

Figure 11: insertion of an β-segment

β ↓	M_α	M_β	$N_{\alpha\alpha}$	$N_{\alpha\beta}$	$N_{\beta\beta}$	$2N_{\beta\beta}+N_{\alpha\beta}$
αα		+1	−1	+2		+2
αβ		+1			+1	+2
βα		+1			+1	+2
ββ		+1			+1	+2

This shows that there are linear relationships of the form

$$2N_{\alpha\alpha} + N_{\alpha\beta} = 2M_\alpha + c_1$$

$$2N_{\beta\beta} + N_{\alpha\beta} = 2M_\beta + c_2$$

The two constants depend on the boundary conditions as can be seen from an inspection of the shortest possible chains with 2 segments. They are zero for periodic boundaries and will be neglected in the following since the numbers M_α, M_β are much bigger.

Figure 12: determination of the constants

	N_α	N_β	$N_{\alpha\alpha}$	$N_{\alpha\beta}$	$N_{\beta\beta}$	$2N_{\alpha\alpha}+N_{\alpha\beta}-2N_\alpha$	$2N_{\beta\beta}+N_{\alpha\beta}-2N_\beta$
α α	2	0	1	0	0	−2	0
β β	0	2	0	0	1	0	−2
α β	1	1	0	1	0	−1	−1
α α (closed)	2	0	2	0	0	0	0
β β (closed)	0	2	0	0	2	0	0
α β (closed)	1	1	0	2	0	0	0

We substitute

$$N_{\alpha\alpha} = M_\alpha - \frac{1}{2}N_{\alpha\beta}$$

$$N_{\beta\beta} = M_\beta - \frac{1}{2}N_{\alpha\beta}$$

$$w = w_{\alpha\alpha} + w_{\beta\beta} - 2w_{\alpha\beta}$$

to have the interaction energy

$$W = w_{\alpha\alpha}(M_\alpha - \frac{1}{2}N_{\alpha\beta}) + w_{\beta\beta}(M_\beta - \frac{1}{2}N_{\alpha\beta}) + w_{\alpha\beta}N_{\alpha\beta}$$

$$= w_{\alpha\alpha}M_\alpha + w_{\beta\beta}(M - M_\alpha) - \frac{w}{2}N_{\alpha\beta}$$

The canonical partition function is

$$Z(M_\alpha, T) = z_\alpha^{M_\alpha} z_\beta^{M_\beta} \sum_{N_{\alpha\beta}} g(M_\alpha, N_{\alpha\beta}) e^{-\frac{W(N_{\alpha\beta})}{kT}}$$

$$= \left(z_\alpha e^{-w_{\alpha\alpha}/kT}\right)^{M_\alpha} \left(z_\beta e^{-w_{\beta\beta}/kT}\right)^{(M-M_\alpha)} \sum_{N_{\alpha\beta}} g(M_\alpha, N_{\alpha\beta}) e^{\frac{N_{\alpha\beta} w}{2kT}}$$

The degeneracy factor g will be evaluated in the following. The figure shows an example.

Figure 14: distribution of 3 segments over 3 blocks is equivalent to arrange 3 segments and 2 border lines

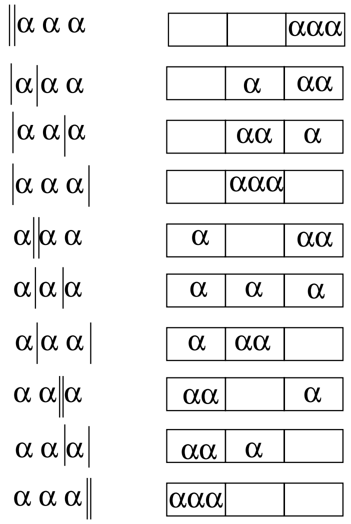
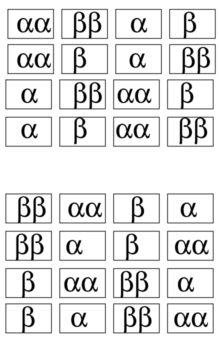


Figure 13: degeneracy g



The chain can be divided into blocks containing only α-segments (α-blocks) or only β-segments (β-blocks). The number of boundaries between α-blocks and β-blocks obviously is given by $N_{\alpha\beta}$. Let $N_{\alpha\beta}$ be an odd number. Then there are $(N_{\alpha\beta}+1)/2$ blocks of each type (We assume that $N_{\alpha\beta}, M_\alpha, M_\beta$ are large numbers and neglect small differences of order 1 for even $N_{\alpha\beta}$). In each α-block there is at least one α-segment. The remaining $M_\alpha - (N_{\alpha\beta}+1)/2$ α-segments have to be distributed over the $(N_{\alpha\beta}+1)/2$ α-blocks .

Therefore we need the number of possible ways to arrange $M_\alpha - (N_{\alpha\beta} + 1)/2$ segments and $(N_{\alpha\beta}-1)/2$ walls which is given by the number of ways to distribute the $(N_{\alpha\beta}-1)/2$ walls over the total of $M_\alpha - 1$ objects which is given by

$$\frac{(M_\alpha - 1)!}{(\frac{N_{\alpha\beta}-1}{2})!(M_\alpha - \frac{N_{\alpha\beta}+1}{2})!} \approx \frac{M_\alpha!}{(\frac{N_{\alpha\beta}}{2})!(M_\alpha - \frac{N_{\alpha\beta}}{2})!}$$

The same consideration for the β-segments gives another factor of

$$\frac{(M - M_\alpha)!}{(\frac{N_{\alpha\beta}}{2})!(M - M_\alpha - \frac{N_{\alpha\beta}}{2})!}$$

Finally there is an additional factor of 2 because the first block can be of either type. Hence for large numbers we find

$$g(M_\alpha, N_{\alpha\beta}) = 2\frac{(M_\alpha)!}{(\frac{N_{\alpha\beta}}{2})!(M_\alpha - \frac{N_{\alpha\beta}}{2})!}\frac{(M - M_\alpha)!}{(\frac{N_{\alpha\beta}}{2})!(M - M_\alpha - \frac{N_{\alpha\beta}}{2})!}$$

We look for the maximum summand of Z as a function of $N_{\alpha\beta}$. The corresponding number will be denoted as $N^*_{\alpha\beta}$ and is determined fromthe condition

$$0 = \frac{\partial}{\partial N_{\alpha\beta}} \ln\left(g(M_\alpha, N_{\alpha\beta})e^{\frac{wN_{\alpha\beta}}{2kT}}\right) = \frac{w}{2kT} + \frac{\partial}{\partial N_{\alpha\beta}} \ln g(M_\alpha, N_{\alpha\beta})$$

Stirlings approximation gives

$$0 = \frac{w}{2kT} + \frac{1}{2}\ln(M_\alpha - \frac{N^*_{\alpha\beta}}{2}) + \frac{1}{2}\ln(M - M_\alpha - \frac{N^*_{\alpha\beta}}{2}) - \ln(\frac{N^*_{\alpha\beta}}{2})$$

or

$$0 = \frac{w}{kT} + \ln\left(\frac{(M_\alpha - \frac{N^*_{\alpha\beta}}{2})(M - M_\alpha - \frac{N^*_{\alpha\beta}}{2})}{(\frac{N^*_{\alpha\beta}}{2})^2}\right)$$

Taking the exponential gives

$$(M_\alpha - \frac{N^*_{\alpha\beta}}{2})(M - M_\alpha - \frac{N^*_{\alpha\beta}}{2}) = e^{-\frac{w}{kT}}\left(\frac{N_{\alpha\beta}}{2}\right)^2$$

which can be btw rewritten as a mass-action law

$$\frac{N_{\alpha\alpha}N_{\beta\beta}}{N^2_{\alpha\beta}} = \frac{e^{-w/kT}}{4}$$

for the chemical reaction

$$2\alpha\beta \rightleftharpoons \alpha\alpha + \beta\beta$$

Introducing the relative quantities

$$\delta = \frac{M_\alpha}{M} \qquad \gamma = \frac{N^*_{\alpha\beta}}{2M}$$

we have to solve the quadratic equation

$$(\delta - \gamma)(1 - \delta - \gamma) = \gamma^2 e^{-\frac{w}{kT}}$$

The solutions are

$$\gamma = \frac{-1 \pm \sqrt{(1-2\delta)^2 + 4e^{-w/kT}\delta(1-\delta)}}{2(e^{-w/kT} - 1)}$$

Series expansion around w=0 gives

$$\gamma = \frac{kT}{2w} + \frac{1}{4} - \frac{w}{24kT} + \cdots \pm \left(-\frac{kT}{2w} + \delta(1-\delta) - \frac{1}{4} \right) + \cdots$$

The - alternative diverges for $w \to 0$ whereas the + alternative approaches the value

$$\gamma_0 = \delta - \delta^2$$

which is the only solution of the interactionless case

$$(\delta - \gamma_0)(1 - \delta - \gamma_0) = \gamma_0^2 \to \delta(1-\delta) - \gamma = 0$$

The physically correct solution can be written as

$$\gamma = \frac{1-\xi}{2(1-e^{-w/kT})}$$

with

$$\xi = \sqrt{(1-2\delta)^2 + 4e^{-w/kT}\delta(1-\delta)}$$

We easily find

$$(1-\xi)(1+\xi) = 1 - (1-2\delta)^2 - 4e^{-w/kT}\delta(1-\delta) = 4\delta(1-\delta) - 4e^{-w/kT}(1-\delta)\delta$$

$$= 4\delta(1-\delta)(1-e^{-w/kT})$$

and hence we can write

$$\gamma = \frac{2\delta(1-\delta)}{(1+\xi)}$$

The physically correct value of $N^*_{\alpha\beta}$ is

$$N^*_{\alpha\beta} = \frac{-M + \sqrt{(M-2M_\alpha)^2 + 4e^{-w/kT}M_\alpha(M-M_\alpha)}}{e^{-w/kT} - 1}$$

Let us now apply the maximum term method which approximates the logarithm of a sum by the logarithm of the maximum summand.

$$F = -kT\ln Z(M_\alpha, T) \approx -kTM_\alpha \ln z_\alpha - kT(M-M_\alpha)\ln z_\beta + M_\alpha w_{\alpha\alpha} + (M-M_\alpha)w_{\beta\beta}$$

$$-kT\ln g(M_\alpha, N^*_{\alpha\beta}) - \frac{wN^*_{\alpha\beta}}{2}$$

The force-length relation is now obtained from

$$\kappa = \frac{\partial F}{\partial L} = \frac{\partial F}{\partial M_\alpha}\frac{\partial(\frac{L-Ml_\beta}{l_\alpha - l_\beta})}{\partial L} = \frac{1}{l_\alpha - l_\beta}\frac{\partial F}{\partial M_\alpha}$$

$$= \frac{1}{l_\alpha - l_\beta}\left(-kT\ln z_\alpha + kT\ln z_\beta + w_{\alpha\alpha} - w_{\beta\beta} - kT\frac{\partial}{\partial M_\alpha}\ln g \right)$$