Chain Statistics

Rules for Constructing the partition function

(a) Consider all the possible conformations (states) of the chain

(b) Establish a reference state and assign it a statistical weight 1

(c) For each conformation that is not the reference state assign a statistical weight

(d) Construct the partition function

Zipper Model:

* Each residue can be in the coil state (c) or the helical state (h).

* In the zipper model two sequences of helices separated by sequence of coils is not allowed; there can be only one sequence of helices.

* The entire sequence of N residues being in the coil state is the reference

Zipper Model

* <u>Nucleation step</u>: The probability of initializing the helical sequence is small; thus, the probability of having a h following a c is small and is given by

$$\sigma s \quad \text{with} \quad \sigma << 1$$

* <u>Propagation step</u>: The probability of propagating an already initiated helical sequence is better than the nucleation step and the probability is given by s.

* The probabilities above are w.r.t having a coil.

As a means of illustrating the rules, the sequence

ccchhhhhccc

has a weight $(\sigma s)(s)(s)(s)(s)$

$$= \sigma s^5$$

Zipper Model

- Consider a sequence of N residues
- Note that there can only a single sequence of contiguous helices.
- This single sequence of contiguous helices can be of length

$$k = 1, 2, 3, \cdots N$$

→ A sequence of contiguous helices of length k can be placed in N long slots is

$$\Omega_k = N - k + 1.$$

→ The probability of all k length helices is

$$\sigma s^k.$$

→ Thus the partition function is given by

$$Z = \sum_{k=1}^{N} \Omega_k \sigma s^k + \underset{\substack{\uparrow \\ \text{for the sequence of all } C\text{'s}}}{1}$$

Zipper Model

Thus we have

$$Z = 1 + \sum_{k=1}^{N} \Omega_k \sigma s^k$$

$$= 1 + \sum_{k=1}^{N} (N-k+1) \sigma s^k$$

Note that $\displaystyle\sum_{k=1}^{N} s^k = \frac{s^{N+1} - s}{(s-1)}$

Thus,

$$Z = 1 + (N+1)\sigma \sum_{k=1}^{N} s^k - \sum_{k=1}^{N} k\sigma s^k$$

$$= 1 + (N+1)\sigma \frac{(s^{N+1} - s)}{s-1} - \sum_{k=1}^{N} k\sigma s^k$$

Now, as

$$\sum_{k=1}^{N} s^k = \frac{s^{N+1} - s}{s-1}$$

$$\Rightarrow \quad \sum_{k=1}^{N} k s^{k-1} = \frac{d}{ds}\left(\frac{s^{N+1} - s}{s-1} \right)$$

Zipper Model

Thus $$\sum_{k=1}^{N} k s^{k-1} = \frac{d}{ds}\left(\frac{s^{N+1}-s}{s-1}\right)$$

$$\Rightarrow \sum_{k=1}^{N} k s^{k} = s\sum_{k=1}^{N} k s^{k-1} = s\,\frac{d}{ds}\left(\frac{s^{N+1}-s}{s-1}\right)$$

$$\Rightarrow \sum_{k=1}^{N} k s^{k} = s\left[-\frac{s^{N+1}-s}{(s-1)^2} + \frac{(N+1)s^{N}-1}{s-1}\right]$$

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

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

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

Thus,
$$Z = 1 + \frac{\sigma s^2}{(s-1)^2}\left[s^{N} + N s^{-1} - (N+1)\right]$$

Zipper Model

Question: What is the probability that the chain has k helical units?

Solution: Let $p(k)$ be the probability that there are k helical units. is

$$\frac{\Omega(k)\,\sigma s^k}{Z}$$

$$= \frac{(N-k+1)\,\sigma s^k}{Z}$$

Question: What is the average value of the length of the helical string

Solution:

$$\langle K \rangle = \sum_{k=1}^{N} k\, p(k)$$

$$= \frac{\sum_{k=1}^{N} k\, \Omega(k)\, \sigma s^k}{Z}$$

$$= \sum_{k=1}^{N} k\,(N-k+1)\,\sigma s^k \Big/ Z$$

Zipper Model

Thus

$$\langle k \rangle = \frac{\sum_{k=1}^{N} (N-k+1) k \sigma s^k}{Z}$$

with $Z = \sum_{k=1}^{N} (N-k+1) \sigma s^k$

$$\therefore \quad \langle k \rangle = s \frac{\frac{\partial}{\partial s}(Z)}{Z}$$

$$\therefore \quad \langle k \rangle = s \frac{\partial}{\partial s}(\ln Z)$$

$$= \left(\frac{\partial \ln Z}{\partial \ln s} \frac{\partial \ln s}{\partial s} \right) s$$

$$= \frac{\partial \ln Z}{\partial \ln s} \cdot \frac{1}{s} s = \frac{\partial \ln Z}{\partial \ln s}$$

$$\therefore \quad \langle k \rangle = \frac{\partial \ln Z}{\partial \ln s}$$

The fractional helicity is defined as

$$\theta = \frac{\langle k \rangle}{N} = \frac{1}{N} \frac{\partial \ln Z}{\partial \ln s}$$

Zipper Model

$$\theta = \frac{\sigma s}{(s-1)^3}\left[\frac{N s^{N+2} - (N+2)s^{N+1} + (N+2)s - N}{N\left\{1 + \left[\frac{\sigma s}{(s-1)^2}\right]\left[s^{N+1} + N - (N+1)s\right]\right\}}\right]$$

Some Conclusions:

→ $\theta = 0$ when $s = 0$

→ $\lim\limits_{s \to \infty} \theta = 1$

For large N

$\theta = 0.5$ occurs when $s = 1$.

Role of σ (the initiation parameter)

(*) Note that the probability of having a helical length k is

$$p(k) = \sigma (N-k+1) s^k.$$

(*) Assume that $s > 1$.

If σ is very-very small then $p(k)$ is appreciable only if k is large. Thus σ small would lead to all helical or no helical sequences; thus, σ small encourages cooperativity.

Zimm-Bragg model

* Note that in the earlier zipper model it was possible to have only one region of helical residues

* The zipper model is therefore a reasonable model for short chains

* A more flexible model is when disjoint helical regions are allowed.

Suppose the chain is N units long.

Again the energetics needs to account for nucleation step and the propagation step. Thus,

* A h following a c has a weight σs

* A h following a h has a weight s

* A c following a c has a weight 0

Zimm-Bragg Model

We need to create the partition function

→ Lets assume that there are a total of k helical units. Suppose these k helical units forms J contiguous helical subchains (separated by coil units).

- The weight of a chain with k total helical units with J distinct helical strings is $(\sigma s)^J s^{k-J}$ where, each of the J helical residues at the begining of each helical subunit has a weight (σs); thus a factor $(\sigma s)^J$; the remaining $(k-J)$ helical units have a weight s.

- The number of ways of partitioning k total helical units into J distinct units is $\Omega_{JK} = {}^{k}C_{J}$ (k choose J).

- The partition function is therefore

$$Z = \sum_{J,k} \Omega_{Jk} (\sigma s)^J s^{k-J}$$

Zimm Bragg model

(4) Thus the probability of having k helical units with J distinct units is

$$p(J,k) = \frac{\mathcal{N}_{J,k} (\sigma s)^J s^{k-J}}{Z}$$

$$= \frac{\mathcal{N}_{J,k} \sigma^J s^k}{Z}$$

This is in general quite hard to calculate.

We will now introduce the matrix method to obtain the partition function.

Matrix Method

With respect to the respective weights $T(i,j)$; $i=-1,1$; $j=1,-1$

Define a matrix

$$T := \begin{bmatrix} T(-1,-1) & T(-1,1) \\ T(+1,-1) & T(1,1) \end{bmatrix}$$

Then lets evaluate the $(i,j)^{th}$ entry of T^2

$$T^2(i,j) = \sum_{S_N=-1}^{1} T(i,S_N)\,T(S_N,j)$$

Now, the $(i,j)^{th}$ entry of T^3 is

$$T^3(i,j) = \sum_{S_{N-1}=-1}^{1} T(i,S_{N-1})\,T^2(S_{N-1},j)$$

$$= \sum_{S_{N-1}=-1}^{1} T(i,S_{N-1})\left[\sum_{S_N=-1}^{1} T(S_{N-1},S_N)\,T(S_N,j)\right]$$

$$T^3(i,j) = \sum_{S_{N-1}=-1}^{1}\sum_{S_N=-1}^{1} T(i,S_{N-1})\,T(S_{N-1},S_N)\,T(S_N,j)$$

Matrix Method

Similarly it follows that

$$T^4(i,j) = \sum_{S_{N-2}=-1}^{1} T(i, S_{N-2})\, T^3(S_{N-2}, j)$$

$$T^4(i,j) = \sum_{S_{N-2}=-1}^{1} T(i, S_{N-2}) \sum_{S_{N-1}=-1}^{1} \sum_{S_N=-1}^{1} T(S_{N-2}, S_{N-1})\, T(S_{N-1}, S_N)\, T(S_N, j).$$

$$\therefore \quad T^2(i,j) = \sum_{S_N=-1}^{1} T(i, S_N)\, T(S_N, j)$$

$$T^3(i,j) = \sum_{S_{N-1}=-1}^{1} \sum_{S_N=-1}^{1} T(i, S_{N-1})\, T(S_{N-1}, S_N)\, T(S_N, j)$$

$$T^4(i,j) = \sum_{S_{N-2}=-1}^{1} \sum_{S_{N-1}=-1}^{1} \sum_{S_N=-1}^{1} T(i, S_{N-2})\, T(S_{N-2}, S_{N-1})\, T(S_{N-1}, S_N)\, T(S_N, j)$$

and therefore by induction it can be shown that

$$T^m(i,j) = \sum_{S_{N-m+2}} \sum_{S_{N-m+2}} \cdots \sum_{S_N} T(i, S_{N-m+2}) \cdots T(S_{N-1}, S_N)\, T(S_N, j)$$

Matrix Method

Thus

$$T^m(i,j) = \sum_{s_{N-m+2}} \cdots \sum_{s_N} T(i, s_{N-m+2}) T(s_{N-m+2}, s_{N-m+2}) \cdots T(s_{N-1}, s_N)\, T(s_N, j).$$

In particular

$$T^N(i,j) = \sum_{s_2} \sum_{s_3} \cdots \sum_{s_N} T(i, s_2)\, T(s_2, s_3)\, T(s_3, s_4) \cdots T(s_{N-1}, s_N)\, T(s_N, j)$$

Now, $\quad \mathrm{Trace}(T^N) = T^N(-1,-1) + T^N(1,1)$

Therefore.

$$\mathrm{Trace}[T^N] = \sum_{s_2 \cdots s_N} T(1, s_2)\, T(s_2, s_3) \cdots T(s_{N-1}, s_N)\, T(s_N, 1) + \sum_{s_2 \cdots s_N} T(-1, s_2) \cdots T(s_N, -1)$$

Matrix Method

Thus

$$T^N(i,j) = \sum_{s_2=-1}^{1} \cdots \sum_{s_N=-1}^{1} T(i,s_2)T(s_2,s_3)\cdots T(s_{N-1},s_N)T(s_N,j)$$

and

if $S_{N+1} = S_1$ then

$$Z := \sum_{S_1} \sum_{S_2} \cdots \sum_{S_N} T(S_1,S_2)\,T(S_2,S_3)\cdots T(S_N,S_{N+1})$$

$$= \mathrm{Trace}\,(T^N).$$

Matrix Method

- Consider the problem of a N sequence of residues each of which can be a h or a c.

- Also, we will assume that there is an element before the first nucleotide which is neccessarily a coil unit c.

Therefore we have a sequence of the form

$$-1\ \delta_1\ \delta_2\ \ldots\ \delta_N$$

where $\delta_i \in \{-1, 1\}$; with the

associated cost

$$T(-1, \delta_1)\, T(\delta_1, \delta_2) \ldots T(\delta_{N-1}, \delta_N).$$

Thus, the partition function in this case is given by

$$\sum_{\delta_1 \ldots \delta_N} T(-1\ \delta_1)\, T(\delta_1, \delta_2) \ldots T(\delta_{N-1}, \delta_N).$$

Zimm Bragg Partition function

$$T^N(i,j) = \sum_{S_2=-1}^{1} \cdots \sum_{S_N=-1}^{1} T(i,S_2)\,T(S_2,S_3) \cdots T(S_{N-1},S_N)\,T(S_N,j)$$

$$= \sum_{S_1=-1}^{1} \cdots \sum_{S_{N-1}=-1}^{1} T(i,S_1)\,T(S_1,S_2) \cdots T(S_{N-1},j)$$

where we have simply changed the notation for the indices.

What we need is

$$\sum_{S_1=-1}^{1} \cdots \sum_{S_{N-1}=-1}^{1} \sum_{S_N=-1}^{1} T(-1,S_1)\,T(S_1,S_2) \cdots T(S_{N-1},S_N)$$

$$= \sum_{S_1 \cdots S_{N-1}} T(-1,S_1) \cdots T(S_{N-2},S_{N-1})\left[T(S_{N-1},-1) + T(S_{N-1},+1)\right]$$

$$= \sum_{S_1,S_2,\ldots S_{N-1}} T(-1,S_1) \cdots T(S_{N-2},S_{N-1})\,T(S_{N-1},-1) + \sum_{S_1,S_2\ldots S_{N-1}} T(-1,S_1) \cdots T(S_{N-2},S_{N-1})\,T(S_{N-1},+1)$$

$$= T^N(-1,-1) + T^N(-1,1) = \begin{bmatrix} T^N(-1,1) & T^N(-1,1) \end{bmatrix} \begin{bmatrix} 1 \\ 1 \end{bmatrix}$$

Zimm Bragg Partition function

Thus

$$Z = \begin{bmatrix} T^N(-1,1) & T^N(-1,1) \end{bmatrix} \begin{bmatrix} 1 \\ 1 \end{bmatrix}$$

$$= \begin{bmatrix} 1 & 0 \end{bmatrix} T^N \begin{bmatrix} 1 \\ 1 \end{bmatrix}$$

Thus, the partition function is

$$Z = \begin{bmatrix} 1 & 0 \end{bmatrix} T^N \begin{bmatrix} 1 \\ 1 \end{bmatrix}$$

with $T = \begin{bmatrix} T(-1,-1) & T(-1,1) \\ T(1,-1) & T(+1,1) \end{bmatrix}$

Matrix Method.

⊛ Lets denote the coil state by -1 and the helical residue by 1

⊛ Then let

$T(-1,1)$ denote the transition weight of a coil to a helical residue
$T(-1,-1)$ denote a cc sequence
$T(1,-1)$ denote a hc sequence
$T(1,1)$ denote a hh sequence

Therefore
$$T(-1,1) = \sigma s$$
$$T(-1,-1) = 1$$
$$T(1,-1) = 1$$
$$T(1,1) = s$$

Thus,
$$T = \begin{bmatrix} 1 & \sigma s \\ 1 & s \end{bmatrix}$$

Matrix Method

Diagonalizing the matrix T will aid in obtaining a closed form solution to the partition function Z.

Note that for the T as described above

$$M^{-1} T M = \begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{bmatrix} =: \Lambda$$

with
$$\lambda_1 = \frac{(1+s) + \sqrt{(1-s)^2 + 4\sigma s}}{2}$$

$$\lambda_2 = \frac{(1+s) - \sqrt{(1-s)^2 + 4\sigma s}}{2}$$

$$M = \begin{bmatrix} 1-\lambda_2 & 1-\lambda_1 \\ 1 & 1 \end{bmatrix} ; \quad M^{-1} = \frac{1}{\lambda_1 - \lambda_2} \begin{bmatrix} 1 & \lambda_1 - 1 \\ -1 & 1-\lambda_2 \end{bmatrix}$$

Closed-form of partition function

It is evident that

$$T^N = M \Lambda^N M^{-1}$$

$$= M \begin{bmatrix} \lambda_1^N & 0 \\ 0 & \lambda_2^N \end{bmatrix} M^{-1}$$

and

$$Z = [1\ 0]\, T^N \begin{bmatrix} 1 \\ 1 \end{bmatrix}$$

$$= \frac{\left[\lambda_1^{N+1}(1-\lambda_2) - \lambda_2^{N+1}(1-\lambda_1)\right]}{\lambda_1 - \lambda_2}$$

As $\lambda_1 > \lambda_2$ it follows that $\lambda_1^{N+1} \gg \lambda_2^{N+1}$ for N large and a good approximation for N large is

$$Z = \frac{\lambda_1^{N+1}(1-\lambda_2)}{(\lambda_1 - \lambda_2)} \text{ for } N \text{ large}$$

Closed form of the partition function.

$\therefore$

$$Z \approx \frac{\lambda_1^{N+1}(1-\lambda_2)}{(\lambda_1-\lambda_2)} \quad \text{for } N \text{ large}$$

and $\ln Z \approx N \ln \lambda_1$

Thus for large number of residues we have

$$Z \approx N \ln \lambda_1$$

with

$$\lambda_1 = \frac{(1+s)+\sqrt{(1-s)^2+4\sigma s}}{2}$$

Statistics using Partition function

We have also expressed the partition function another way.

* Assume that out of N residues there are k helical units, with J separate contiguous helical strings. Each such chain of residues has a weight

$$(\sigma s)^J s^{k-J} = \sigma^J s^k$$

* Let there be $\Omega_{J,k}$ such chains then the partition function is given by

$$Z = \sum_{J,k} \Omega_{J,k} (\sigma^J s^k)$$

* The probability of having k helical units with J distinct helical subchains is

$$p(J,k) = \frac{\Omega_{J,k}\, \sigma^J s^k}{Z}$$

Statistics Using Partition function

$$p(J,k) = \frac{\Omega_{J,k}\,\sigma^J s^k}{Z}$$

Now, probability that there are k helical units in the chain is

$$p(k) = \sum_J p(J,k) = \frac{\sum_J \Omega_{J,k}\,\sigma^J s^k}{Z}$$

$$\langle k \rangle = \sum_k k\,p(k)$$

$$= \frac{\sum_k \sum_J k\,\Omega_{J,k}\,\sigma^J s^k}{Z}$$

Now $Z = \sum_{k,J} \Omega_{J,k}\,\sigma^J s^k$

$$\frac{\partial Z}{\partial s} = \sum_{k,J} \Omega_{J,k}\,\sigma^J k\,s^{k-1}$$

and $\frac{1}{Z}\frac{\partial Z}{\partial s} = \frac{\sum_{k,J} \Omega_{J,k}\,\sigma^J k\,s^{k-1}}{Z}$

$$\therefore s\,\frac{\partial \ln Z}{\partial s} = \frac{\sum_{k,J} \Omega_{J,k}\,\sigma^J k\,s^k}{Z} = \langle k \rangle$$

Fractional Helicity

Thus

$$\langle k \rangle = s \frac{\partial \ln Z}{\partial s}$$

Now, if the number of residues in the chain are large then

$$\ln Z \simeq N \ln \lambda_1 \quad \text{with}$$

$$\lambda_1 = \frac{(1+s) + \sqrt{(1-s)^2 + 4\sigma s}}{2}$$

$$\therefore \frac{\langle k \rangle}{N} = \frac{s}{2\lambda_1} \left\{ 1 + \frac{(s-1) + 2\sigma}{\sqrt{(s-1)^2 + 4\sigma s}} \right\}$$

$\therefore$ fractional helicity is

$$\theta = \frac{s}{2\lambda_1} \left\{ 1 + \frac{(s-1) + 2\sigma}{((s-1)^2 + 4\sigma s)^{1/2}} \right\}$$

Suppose $\sigma \ll 1$ and $(s-1) > \varepsilon$ with $\varepsilon \sim O(1)$ then

$$\theta = \frac{1+\varepsilon}{2\lambda_1} \left\{ 1 + \frac{s-1}{|s-1|} \right\} = \frac{1+\varepsilon}{2\lambda_1} \{ 1 + 1 \} \simeq 1 \quad \text{as } \lambda_1 \simeq 1$$

Fractional Helicity

If $S = 1-\varepsilon$ with $\varepsilon > 1$

Then

$$\Theta = \frac{S}{2\lambda_1}\left\{1 + \frac{S-1}{|S-1|}\right\}$$

$$= \frac{1-\varepsilon}{2}\left\{1 + \frac{1-\varepsilon-1}{|1-\varepsilon-1|}\right\}$$

$$= \frac{1-\varepsilon}{2}\left\{1 - 1\right\} \cong 0.$$

$\therefore$ For s large and positive

$$\Theta \cong 1$$

and for $|s|$ large and negative

$$\Theta \simeq 0.$$

Sharpness of Transition

Let $0 < \sigma << 1$

We will now obtain an estimate of the width of the transition.

$$\theta = \frac{s}{2\lambda_1}\left\{1 + \frac{(s-1)+2\sigma}{((s-1)^2+4\sigma s)^{1/2}}\right\}$$

(*) Suppose $s = 1-\varepsilon$ with $\varepsilon > 0$ small and such that

$$(s-1)^2 \gg 4\sigma$$

$$\Rightarrow \quad \varepsilon^2 \gg 4\sigma$$

It follows that

$$\varepsilon \gg 2\sigma^{1/2} \quad \text{and} \quad \varepsilon \ggg 2\sigma$$

Thus, let $0 < 2\sigma^{1/2} << \varepsilon << 1$.

$$\theta = \frac{1-\varepsilon}{2\lambda_1}\left\{1 + \frac{-\varepsilon+2\sigma}{\{\varepsilon^2+4\sigma(1-\varepsilon)\}^{1/2}}\right\}$$

$$= \frac{1-\varepsilon}{2\lambda_1}\left\{1 + \frac{-\varepsilon+2\sigma}{\{\varepsilon^2+4\sigma\}^{1/2}}\right\}$$

$$\approx \frac{1-\varepsilon}{2\lambda_1}\left\{1 + \frac{-\varepsilon}{|\varepsilon|}\right] \approx 0$$

Sharpness of Transition

Now
Suppose $0 < 2\sigma^{1/2} << \varepsilon << 1$

and $s = 1+\varepsilon$; then

$$\theta = \frac{s}{2\lambda_1}\left\{1 + \frac{(s-1)+2\sigma}{\{(s-1)^2 + 4\sigma s\}^{1/2}}\right\}$$

$$= \frac{1+\varepsilon}{2\lambda_1}\left[1 + \frac{\varepsilon + 2\sigma}{\{\varepsilon^2 + 4\sigma s\}^{1/2}}\right]$$

$$\approx \frac{1+\varepsilon}{2\lambda_1}\left\{1 + \frac{\varepsilon}{\varepsilon}\right\} \simeq \frac{1+\varepsilon}{2\lambda_1} \cong \frac{2}{2} = 1$$

$\therefore \lambda_1 \simeq 1$ if $s \cong 1$.

Thus, if $s < 1-\varepsilon$ then

$\theta \approx 0$ and

if $s > 1-\varepsilon$ then $\theta = 1$.

with $\varepsilon \approx 2\sigma^{1/2}$.

Sharp Transition of fractional helicity

$\therefore$ θ transitions from a value of 0 to 1 with the range of

$s \in [1-2\sigma^{1/2}, 1+2\sigma^{1/2}]$

which is a very sharp transition.

Thus almost all residues are helical for $s > 1+2\sigma^{1/2}$ and almost all residues are coil for $s < 1-2\sigma^{1/2}$

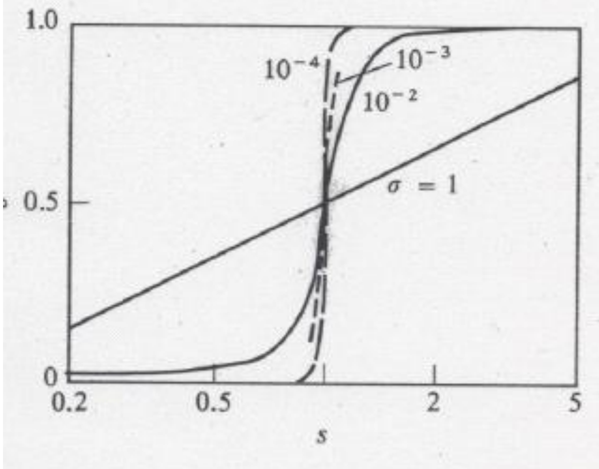

Figure 20-11

Sharpness of transition. The calculated fractional helicity θ is plotted against s (on a natural logarithm scale) for various values of σ. [After B. H. Zimm and J. K. Bragg, *J. Chem. Phys.* 31:526 (1959).]

Taken from the book Cantor and Schimmel

The midpoint of transition occurs at $s = 1$.

Average number of distinct helical segments

We have seen that the probability of finding k helical units with J distinct helical segments is given by

$$p(J,k) = \frac{\Omega_{J,k}\,\sigma^J s^k}{Z}$$

with

$$Z = \frac{\sum_{J,k} \Omega_{J,k}\,\sigma^J s^k}{Z}$$

Therefore probability of finding J distinct helical segments is

$$p(J) = \sum_k p(J,k) = \frac{\sum_k \Omega_{J,k}\,\sigma^J s^k}{Z}$$

and

$$\langle J \rangle = \sum_J J\,p(J,k) = \frac{\sum_{k,J} J\,\Omega_{J,k}\,\sigma^J s^k}{Z}$$

Therefore

$$\langle J \rangle = \frac{\sigma}{Z}\frac{\partial Z}{\partial \sigma}$$

$$= \sigma\frac{\partial \ln Z}{\partial \sigma} = \frac{\partial \ln Z}{\partial \ln \sigma}$$

Average number of helical Segments

Using the approximation that

$\ln Z \simeq N \ln \lambda_1$ for large N we have

$$\langle J \rangle = \frac{N \sigma s}{\lambda_1 \left[(1-s)^2 + 4\sigma s \right]^{1/2}}$$

Thus Average number of helical Segments is

$$\langle J \rangle = \frac{N \sigma s}{\lambda_1 \left[(1-s)^2 + 4\sigma s \right]^{1/2}} .$$

The maximum of $\langle J \rangle$ with respect to s occurs at $s = 1$ where

$$\langle J \rangle_{max} = \frac{N}{2} \sigma^{1/2} .$$

(a) For typical values of $\sigma \simeq 10^{-4}$

$$\langle J \rangle_{max} = \frac{N}{2} 10^{-2} = \frac{N}{200} .$$

Average length of the helical Sequence

We have Seen that the fractional helicity

$$\theta = \frac{s}{2\lambda_1}\left\{1 + \frac{(s-1)+2\sigma}{((s-1)^2+4\sigma s)^{1/2}}\right\}$$

at $s=1$ we have

$$\theta = \frac{1}{2} \Rightarrow \frac{\langle k\rangle}{N} = \frac{1}{2}$$
$$\Rightarrow \langle k\rangle = \frac{N}{2}$$

Thus at $s=1$; the average number of helics residues out of a total of N residues is $\frac{N}{2}$ and the average number of distinct helical strands is $\langle J\rangle = \frac{N}{200}$.

Thus, an estimate of average length

$$= \frac{\text{average \# of helical residues}}{\text{average \# of helical strands}}$$
$$= \frac{\langle k\rangle}{\langle J\rangle} = \frac{N}{2}\cdot\frac{200}{N} = 100$$

Thus, the average length is 100 irrespective of the number of residues. Thus one can conclude that exact phase transition is not possible.