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THE HELIX-COIL TRANSITION BASED ON CORRELATED WALKS

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ABSTRACT.- The helix-coil transition in polypeptides is treated on the basis of the correlated walk model. The model accounts for the physical shape (helix or coil) and the hydrogen bonding. The statistical mechanical calculations reproduce the essential features of the Zimm-Bragg theory. In addition, the nucleation factor σ in the latter theory is related to the turn probability of the polymer segments, and therefore can be calculated within the model. A clear picture of the origin of the nucelation term, which represents the difficulty of forming a first turn of a helix, emerges. The theory, applied to a DNA, predicts a sharper phase transition, which is in agreeement with the experimental observation.

1. INTRODUCTION

In 1959 Zimm and Bragg (Z-B) published a classic paper on the helix-coil transition in polypeptides in terms of the solutions of a modified Ising chain[1]. This theory describes the qualitative features of the phase transition very well. In particular, the narrow temperature range usually observed for the transition is accounted for by the smallness of the nucleation parameter σ. Recently we proposed a theory of the conformation of a polymer with no hydrogen-bonding, based on the correlated walk model[2]. Extending this model with inclusion of the hydrogen-bonding, we propose a new model of a polymer capable of the helix-coil transition. This generalized model contains the Z-B model as a special

case if we look only at the hydrogen-bonding states of each α-amino acid residue -NH-CHR-CO- but it incorporates the physical shape, that is, the helical and coil states of the polymer as well.

The approximate solution suitable for dealing with the helix-coil transition has been obtained in terms of the solutions of modified linear correlated walk. The main features of our results are as follows:

(a) the Z-B theory is recovered;

(b) the initiation of a helical turn, which is characterized by the nucleation parameter σ in the Z-B model, can be discussed and computed in terms of the correlated walk parameters;

(c) a sharper transition is obtained for DNA than for polypeptides.

2. THE MODEL.

Let us consider a polypeptide, H-(NH-CHR-CO)$_n$-OH, where n is the number of amino acid residues.

The conformation of the polymer in solution will be represented by a model-polymer stretched over on a simple cubic lattice with the following rules: a segment follows the direction of the preceding segment with probability α or turns at right angles (four possibilities) with probability γ but does not reverse. The probabilities are normalized such that $\alpha + 4\gamma = 1$.

The lattice constant a_o will be chosen to equal the average linear size of the unit amide residue. In a coil state, the average global shape of the polymer will be characterized in terms of the parameters (α, γ) and a_o. In particular, the mean square end-to-end distance for a model-polymer is calculated to be[2]

$$\frac{\langle R^2\rangle}{a_o^2} = \frac{1+\alpha}{1-\alpha}\, n - \frac{2\alpha(1-\alpha^n)}{(1-\alpha)^2} \qquad (1)$$

Let us now consider the effect of the hydrogen bonding. In the Pauling-Corey alpha-helix structure, each amide (CONH) is hydrogen-bonded to the carbonyl oxygen of the third following amide group. In a helical state 3.6 successive segments form a loop around the helical axis. We will represent this state by a closed correlated path describing a square . We further assume that the hydrogen-bonding is attained only when a segment completes a square with the preceding three segments. This completes our model.

If the hydrogen-bonding state of the model-polymer is looked at, it will be represented by a sequence such as 000111110000011 ... where the digit 1 represents a bonded segment and the digit 0 an unbonded segment. The first three segments are always unbonded and no sequence of less than three 0's should appear by construction. This is in complete agreement with the original Z-B model.

3. THE HELIX-COIL TRANSITION

Our model clearly contains two extreme states: random coil and helical states. Let us now look at the transition between the two. The analysis of the original model is far too complicated as it stands. We will now reduce it to a manageable model.

Let us take a model-polymer with several repeated squares representing helical loops. We will look at it, four successive segments collectively from one end. Each unit of the four may either form a square or not. The state of the $j^{\underline{th}}$ unit will be represented by

$$\mu_j = \begin{matrix} 1 & \text{for closed square (loop)} \\ -1 & \text{for open.} \end{matrix} \tag{2}$$

The statistical weight of a given state $\{\mu_j\}$ of the chain of units is now assumed to be the product of the following factors:

(1) the loop formation factor p if $\mu_j = 1$,

(2) the factor $q = 1-p$ if $\mu_j = -1$,

(3) the Boltzmann factor $\exp(\beta K)$ if a loop follows another loop and unity otherwise; the energy K represent the bond energy between the units.

The loop formation factor p is prescribed to account for the fact that the segments in the unit must proceed in a well-defined orientation to close a square. This factor therefore may be chosen as

$$p = \gamma^4 \quad . \tag{3}$$

The total bond energy may be expressed by the Hamiltonian

$$H = -K \sum_j f(\mu_{j-1}, \mu_j), \tag{4}$$

where

$$f(\mu_1, \mu_2) = \frac{1}{4}(1-\mu_1)(1-\mu_2) = \begin{cases} 1 & \text{if } \mu_1 = \mu_2 = 1 \\ 0 & \text{otherwise.} \end{cases} \tag{5}$$

The above assumption about the statistical factors constitute a highly simplified representation of the problem. In particular, a partially formed square followed by a complete closed square can get no benefit of bonding in this simplified model. A theory improved upon this point will be reported elsewhere.

The partition function Z for this simplified model can be obtained simply, using the standard Ising languages[3]. The transfer matrix T is given by

$$T = \begin{pmatrix} q & q \\ p & pe^{\beta K} \end{pmatrix} \quad . \tag{6}$$

The largest root of the characteristic equation

$$|T - \lambda| = 0 \tag{7}$$

is given by

$$\lambda_o = \frac{1}{2}\left[1 + s + \sqrt{(1-s)^2 + 4t}\right] \quad , \tag{8}$$

where $t \equiv p/q$ and $s \equiv t \exp(\beta K)$ is the ratio of the helix contribution to the partition function to the coil contribution.

In the limit of large n, the free energy ψ per unit is given by

$$\psi = - kT \ln \lambda_o \ . \tag{9}$$

The average degree of helicity, that is, the ratio of the number of helical loops to the total number of units, is

$$\langle f \rangle \equiv \frac{\partial \ln \lambda_o}{\partial(\beta K)} = \frac{s}{\lambda_o}\frac{\lambda_o - 1}{2\lambda_o - s - 1} \quad . \tag{10}$$

This quantity is plotted in Fig. 1 as a function of s.

For smaller values of the loop formation factor p (or t), the transition, which occurs around s = 1, becomes more and more abrupt. A reasonable fit with the experimental observations of Doty and Yang[4] on poly-γ-benzyl-L-glutamate, which are indicated by dots, can be obtained for $t = 2 \times 10^{-4}$.

The results obtained have great similarities to those explicitly worked out by Zimm and Bragg. In fact, if the factor t is replaced by the nucleation term σs in (8), their results follow. The two results for the average degree of helicity are indistinguishable from each other for small values of $t = p(10^{-2}$ or less). This leads to an interpretation that the loop formation factor t essentially characterizes the difficul-

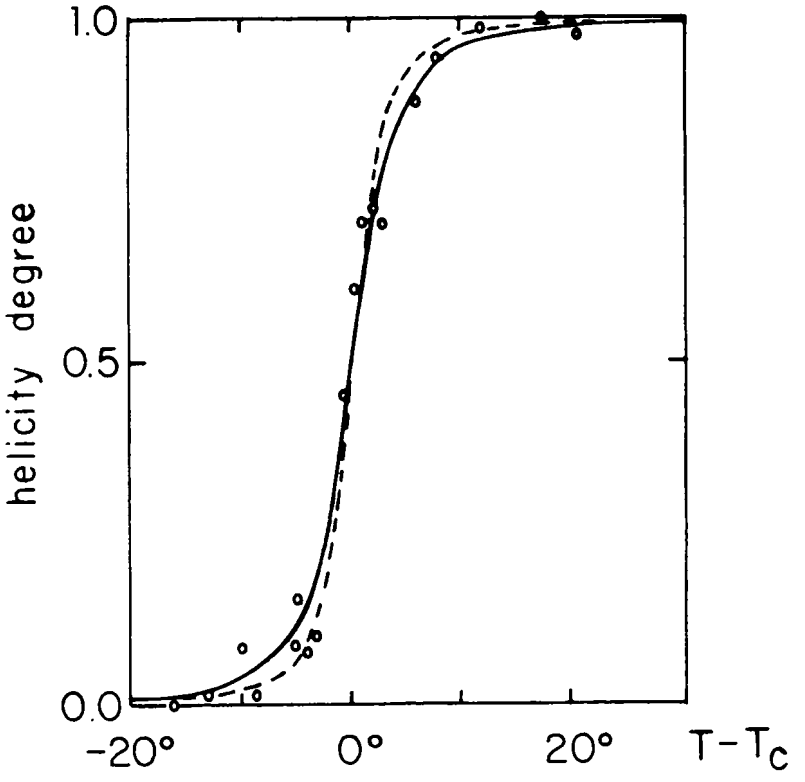

Fig. 1. Theoretical curves of the helicity degree for two t values: ——$t=2 \times 10^{-4}$; --- $t = 1 \times 10^{-4}$. The dots stand for experimental results of optical rotation obtained by Doty and Young[4].

ty of forming an initial loop, that is, the nucleation of a helix. In summary, almost the same results are obtained from the two methods. Since our model contains the physical shape (helix or coil) explicitly, a clearer picture of the nucleation emerges.

The foregoing model and calculations may be applied with a slight modification to the DNA. Since the DNA has double strands, the loop formation factor will be quadratic in p. This factor will therefore be much smaller for DNA. Besides, the bases forming the double helix are more complicated, and this fact also should reduce the factor p. In order to treat this case we start with the following model Hamiltonian:

$$H = -\frac{K}{16}\sum_j (1-\mu_j)(1-\mu_{j+1})(1-\nu_j)(1-\nu_{j+1}) , \qquad (11)$$

where (μ_j, ν_j) are the state variables of the $j^{\underline{th}}$ pair of units. The largest eigenvalue of the corresponding characteristic equation is

$$\lambda_o = \frac{(1 + 2t)}{2}\left[1 + s + \sqrt{(1-s)^2 + 4t^2/(1 + 2t)} \right], \qquad (12)$$

where $s = t^2 e^{\beta K}/(1 + 2t)$. (13)

This yields an even more abrupt phase transition around $s = 1$. This is in agreement with the experimental observation. The melting curves for DNA show a transition with a temperature range of a few degrees in °C while the corresponding temperature range for α-helix extends typically more than five degrees[5]. Since the factor $t \sim p$ is expected to be independent of temperature and base-spices, the melting temperature T_m, determined from $s = 1$, should be proportional to the average bond energy per helix K, which linearly depends on the content of G-C base pairs. This feature also is in agreement with experimental data[5].

It is known that a purely one-dimensional system cannot undergo a sharp phase transition[6]. In our simplified model, the smallness of the loop formation factor p generates a smooth but sharp transition between helix and coil. This factor p was expressed in terms of the turn probability γ as $p = \gamma^4$. If a hypothetical loop contained a large number k of segments, $p = \gamma^k$ would have followed. Since γ is considerably smaller than unity, the factor p would rapidly approach zero for a large k. In this limit, we would have an extremely sharp transition. This is not a contradiction. In fact, an infinitely large helix is a true two-dimensional system, and such a system can undergo an infintely sharp phase transition.

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