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Real-Space Renormalization Group Treatment of Conformational Transitions in Polymers with Long-Range Interactions

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ABSTRACT: The one-dimensional Ising model with nearest-neighbor (or short-range) interactions is often cited as a textbook example of the exact application of the renormalization group procedure for understanding phase transitions and critical phenomena (for short-range models the critical temperature is absolute zero, and there is no true phase transition at finite temperature). By a simple translation of parameters this model describes conformational transitions in polymers. We review the application of the method to the helix–coil transition in polyamino acids and use the method to treat a simple model for polyethylene. We then introduce arbitrarily long-range interactions appropriate for a simple model of DNA, which is of interest because the model exhibits a true phase transition at finite temperatures. The nature of the renormalization group process for this model is explored.

1. Introduction

Recently Li and Scheraga[1] presented a renormalization group treatment of the helix–coil transition in polyamino acids. They made two interesting points. First they noted that one can use the renormalization group procedure as a tool to calculate the free energy of the system (the renormalization group procedure becomes an algorithm to calculate the appropriate eigenvalues when the partition function is expressed as a matrix product). Second, they raised the question as to whether the renormalization group procedure might be useful in protein conformational studies since the renormalization group procedure successively eliminates degrees of freedom producing an equivalent, simplified system.

Exactly how to apply the approach of successive simplifications to proteins is unclear, but the possibility is interesting. One ingredient must be the introduction of long-range interactions. In the present work we extend the work of Li and Scheraga to a model containing arbitrarily long-range interactions in an effort to extend our understanding of the renormalization group procedure in polymers. The model we treat will not be a protein model but rather a simple model for the helix–coil transition in DNA; the model is of interest because, in the limit of infinite chains, it exhibits a true phase transition.

In section 2 we will review two ways to apply the renormalization group method to systems where the partition function can be written as a matrix product. As an example we will review the renormalization group treatment for the Zimm–Bragg model of the helix–coil transition in polyamino acids (the equivalent of the nearest-neighbor Ising model for the magnet). We will then apply the method to models for polyethylene and for the binding of Mg^{2+} ions to DNA in section 3. The DNA model will be discussed in section 4 followed by a brief discussion in section 5.

2. General Technique

Since the original work of Wilson and Wilson and Fisher there have appeared many reviews[2] on the use of the renormalization group to treat phase transitions and critical points. In addition, the ϵ-expansion method of Wilson and Fisher has been extensively applied by de Gennes and Freed[3] to polymers. The case of the nearest-neighbor Ising model has been used many times in texts as a simple exact example of the renormalization group procedure.[4,5] We will briefly review the ideas that we need. We will follow closely the paper by Nelson and Fisher[6] on one-dimensional systems and the work by Li and Scheraga.[1]

For concreteness we will consider a model where there are two conformational states per unit, designated 0 and 1. Thus a typical conformation might be described by the sequence of states

$$0\,0\,0\,0\,0\,1\,1\,1\,0\,0\,1\,1\,1\,1\,1\,0\,1\,0\,0\,0\,1\,1\,1\,1 \tag{1}$$

(The generalization to the case of more than two conformational states per unit is straightforward; we will require three states per unit in our model for polyethylene.) We will take the "0" state as the zero of free energy and assign Boltzmann factors 1 and s to "0" and "1" states, respectively, the Boltzmann factor s reflecting the free energy of a 1 state relative to a 0 state. We require an additional Boltzmann factor, designated σ, that reflects the fact that the border between the two kinds of sequences (runs of 1's and runs of 0's) will in general be unfavorable; hence σ acts as a nucleation parameter for the introduction of a new sequence of 0's. The σ factor might depend on the length of a sequence of 0's (it will in the model for DNA). A sample sequence is shown below with the appropriate Boltzmann factors assigned (all the 0's have factors of 1 that are not shown)

$$\begin{array}{cccccccccccccccc} \ldots & 1 & 1 & 1 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 1 & 1 & 1 & 1 & \ldots \\ & s & s & s & & \sigma_3 & & s & s & & \sigma_2 & s & s & s & s & \end{array} \tag{2}$$

For the special case that the σ_n are independent of n (the length of a sequence of 0's) the model reduces to the standard Zimm–Bragg model[7] for the helix–coil transition in polyamino acids (a nearest-neighbor Ising model). Extensive discussions of the helix–coil transition in biopolymers are given elsewhere.[8,9] With a special choice of the σ_n the model is a simple DNA model, which we will treat in section 4. The same "σ–s" notation can be used to describe other models, as illustrated in the next section. We will restrict ourselves in this section to the nearest-neighbor model with Zimm–Bragg parameters σ and s.

In the renormalization group process it is necessary to introduce another parameter, one that simply scales the free energy of all of the units in the polymer chain. Following Li and Scheraga[1] we will use the symbol r to designate this Boltzmann factor. A sample configuration would then have the assignments of Boltzmann factors

$$\begin{array}{cccccccccccccccc} \ldots & r & r & r & r & r & r & r & r & r & r & r & r & r & r & \ldots \\ \ldots & 1 & 1 & 0 & 0 & 0 & 1 & 1 & 1 & 1 & 1 & 0 & 1 & 0 & 0 & \ldots \\ & s & s & & \sigma & & s & s & s & s & s & \sigma & s & & \sigma & \end{array} \tag{3}$$

for a net factor of $r^{14}s^8\sigma^3$. Since multiplying all of the states by a common factor does not alter any of the statistics of the conformational transition (i.e., averages such as the average amount of helix or the average length of a helix

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sequence), the r factor is generally left out of calculations of the partition function. In the renormalization group procedure it must be included.

We will use a transfer matrix[7-9] $\mathbf{W}$ to assign the proper Boltzmann factors to the states of the chain. For a cyclic chain of N units the partition function is given by

$$Z(r;\sigma,s) = \mathrm{Tr}\mathbf{W}(r;\sigma,s)^N = \sum_{i=1}^{n}\lambda_i(r;\sigma,s)^N \tag{4}$$

where n is the size of the matrix required to treat a particular model and the λ_i are the eigenvalues of $\mathbf{W}$ (we assume that $\mathbf{W}$ can be diagonalized). The requirement that the chain be cyclic is not necessary, but it simplifies the mathematics; at any rate, we will only be interested in the limit of very large N where the value of the partition function is dominated by the largest eigenvalue, λ_1. The essence of the renormalization group method is to reduce the number of degrees of freedom in the model and at the same time assign new statistical weights r', σ', and s'. Here we reduce the number of units in the chain from N to $N/2$ (one could choose $N/3$, $N/4$, etc.). Then one has

$$Z(r';\sigma',s') = \mathrm{Tr}(\mathbf{W}(r';\sigma',s'))^{N/2} = \sum_{i=1}^{n}(\lambda_i(r';\sigma',s'))^{N/2} \tag{5}$$

where $\mathbf{W}'$ is a new transfer matrix (it has the same structure as $\mathbf{W}$ but contains a new set of parameters r', σ', and s'). One can obtain the form of eq 5 from eq 4 as follows:

$$Z(r;\sigma,s) = \mathrm{Tr}(\mathbf{W}(r;\sigma,s))^{N/2} = \sum_{i=1}^{n}(\lambda_i''(r;\sigma,s))^{N/2} \tag{6}$$

The renormalization group requirement is that the partition function remain unchanged in the process $N \rightarrow N/2$

$$Z(r';\sigma',s') = Z(r;\sigma,s) \tag{7}$$

which means that the eigenvalues of $\mathbf{W}'(r';\sigma',s')$ are the same as those of $\mathbf{W}(r;\sigma,s)^2$, i.e.

$$\lambda_i'(r';\sigma',s') = \lambda_i''(r;\sigma,s) = \lambda_i(r;\sigma,s)^2 \tag{8}$$

Equation 8 defines a mapping from the original set of parameters $(r;\sigma,s)$ to a new set $(r';\sigma',s')$ which we can symbolically represent as the renormalization group transformation

$$(r';\sigma',s') = \mathbb{R}(r;\sigma,s) \tag{9}$$

or leaving out the parameter r

$$(\sigma',s') = \mathbb{R}(\sigma,s) \tag{9a}$$

In eq 4–8 we have set the parameter r off with a semicolon to indicate that it has a trivial appearance in $\mathbf{W}$ and λ, i.e.

$$\begin{aligned} \mathbf{W}(r;\sigma,s) &= r\mathbf{W}(\sigma,s) \qquad & \mathbf{W}'(r';\sigma',s') &= r'\mathbf{W}'(\sigma',s') \\ \lambda_i(r;\sigma,s) &= r\lambda_i(\sigma,s) \qquad & \lambda_i'(r';\sigma',s') &= r'\lambda_i'(\sigma',s') \\ & \lambda_i''(r;\sigma,s) = r^2\lambda_i''(\sigma,s) \end{aligned} \tag{10}$$

The crucial mapping is from (σ,s) to (σ',s'), which in general will be found to be independent of the mapping $r \rightarrow r'$ (but the mapping $r \rightarrow r'$ does depend on the mapping $(\sigma,s) \rightarrow (\sigma',s')$). Since all of the physics of the transformation is in the (σ,s) mapping, one might wonder why the parameter r is included at all since it simply scales the free energy of the model; in fact, the equivalence of eq 7 can only be obtained if one includes a change in the scale factor $r \rightarrow r'$.

There are two ways to guarantee that the eigenvalues of the matrix $\mathbf{W}'$ and the matrix $\mathbf{W}^2$ are the same. The first is to simply make all of the elements of one matrix equal to the elements of the other. This is the method used by Nelson and Fisher.[6] The other method is to form the appropriate secular equation from each matrix and then to equate the coefficients of like powers of λ; this is the method used by Li and Scheraga.[1] The element-by-element method gives one more information (more relations between parameters, enabling one to treat models with more parameters) than the secular equation method, but the secular equation method is simpler and allows one to treat transfer matrices of rather complicated structure. We will briefly compare the two methods.

To use the method of direct equivalence of the elements of the matrix, one requires that $\mathbf{W}'$ have the same symmetry and structure as the matrix $\mathbf{W}$ (it represents the same model, just with alternate parameters σ' and s'). Thus to equate matrix elements, $\mathbf{W}'$ and $\mathbf{W}^2$ must have the same symmetry. This is true for the nearest-neighbor Ising model but is not in general true for the other models we want to treat (the problem is that the matrix $\mathbf{W}$ contains zero elements intrinsic to the logic of the model; on squaring $\mathbf{W}$ to form $\mathbf{W}^2$, the locations of the zeros are changed or the zeros are removed altogether). In fact, one does not require the element-by-element equivalence of $\mathbf{W}'$ with $\mathbf{W}^2$ but the equivalence of the eigenvalues. Employing the appropriate similarity transformations, one has ($\mathbf{A}'$ has the same structure as $\mathbf{A}$ but with the primed variables)

$$\begin{gathered} \mathbf{A}\mathbf{W}\mathbf{A}^{-1} = \Lambda \qquad \mathbf{A}\mathbf{W}^2\mathbf{A}^{-1} = \Lambda^2 \qquad \mathbf{A}'\mathbf{W}'(\mathbf{A}')^{-1} = \Lambda' \\ \Lambda' = \Lambda^2 \end{gathered} \tag{11}$$

where the λ values are the appropriate diagonal matrices of eigenvalues. Thus one requires the equivalence

$$\mathbf{A}\mathbf{W}^2\mathbf{A}^{-1} = \mathbf{A}'\mathbf{W}'(\mathbf{A}')^{-1} \tag{12}$$

The elements of $\mathbf{A}$ and $\mathbf{A}'$ will be functions of σ and s and σ' and s', respectively, so eq 12 defines a mapping as in eq 9. But in general, this is a rather involved procedure.

In the method of secular equations one forms the general equation for the two appropriate secular equations

$$\begin{gathered} |\mathbf{W}'(r';\sigma',s') - \lambda'\mathbf{I}| = 0 \\ |\mathbf{W}^2(r;\sigma,s) - \lambda''\mathbf{I}| = 0 \end{gathered} \tag{13}$$

or

$$\begin{gathered} |r'\mathbf{W}'(\sigma',s') - \lambda'\mathbf{I}| = 0 \\ |r^2\mathbf{W}^2(\sigma,s) - \lambda''\mathbf{I}| = 0 \end{gathered} \tag{14}$$

These equations are then expanded to give the polynomials

$$\begin{gathered} (\lambda')^n + (r')P_{n-1}(\lambda')^{n-1} + (r')^2P_{n-2}(\lambda')^{n-2} + \ldots + (r')^nP_0 = 0 \\ (\lambda'')^n + (r^2)Q_{n-1}(\lambda'')^{n-1} + (r^2)^2Q_{n-2}(\lambda'')^{n-2} + \ldots + (r^2)^nQ_0 = 0 \end{gathered} \tag{15}$$

The condition that the eigenvalues of both are equivalent is that the coefficients of like powers of λ be equal

$$(r')^mP_{n-m}(\sigma',s') = (r^2)^mQ_{n-m}(\sigma,s) \tag{16}$$

for $m = 0$ to $n - 1$ (n equations). The r's can be eliminated by forming ratios

$$\frac{P_{n-m}(\sigma',s')}{P_{n-1}(\sigma',s')^m} = \frac{Q_{n-m}(\sigma,s)}{Q_{n-1}(\sigma,s)^m} \tag{17}$$

There are $n - 1$ such equations; an nth equation determines the value of r'.

Since the polynomials of eq 15 will be our key relations, it is useful to simplify the notation. We define

$$u_m = (\lambda')^m(r')^{n-m}; \qquad v_m = (\lambda'')^n(r^2)^{n-m} \tag{18}$$

Then eq 15 becomes

$$u_n + P_{n-1}u_{n-1} + P_{n-2}u_{n-2} + \ldots + P_0u_0 = 0$$
$$v_n + Q_{n-1}v_{n-1} + Q_{n-2}v_{n-2} + \ldots + Q_0v_0 = 0 \qquad (19)$$

The DNA model with long-range interactions reduces to the nearest-neighbor model when all of the σ_n are independent of n. Thus it is useful to begin by examining the behavior of this limiting case; it will also allow us to illustrate the two different methods of obtaining the renormalization group transformation and to see the advantages and disadvantages of each method. To assign statistical weights (Boltzmann factors) for the nearest-neighbor model illustrated in (3) we require the following transfer matrix, which correlates the states of a general unit i in the chain (row indices) with the states of the following unit, $i + 1$ (column indices):

$$\begin{array}{cc} & \begin{array}{cc} 1 & 0 \end{array} \\ \begin{array}{c} 1 \\ 0 \end{array} & \begin{bmatrix} s & (\sigma s)^{1/2} \\ (\sigma s)^{1/2} & 1 \end{bmatrix} \end{array} \qquad (20)$$

By assigning $(\sigma s)^{1/2}$ to all 10 and 01 boundaries one assigns a net factor of σ to each sequence of zeroes; the form of (20) is chosen to give a symmetric matrix. The transfer matrices $\mathbf{W}$ and $\mathbf{W}'$ are then

$$\mathbf{W} = \begin{bmatrix} s & (\sigma s)^{1/2} \\ (\sigma s)^{1/2} & 1 \end{bmatrix} \qquad \mathbf{W}' = \begin{bmatrix} s' & (\sigma' s')^{1/2} \\ (\sigma s')^{1/2} & 1 \end{bmatrix} \qquad (21)$$

The renormalization group process requires an equivalence as follows:

$$r^2\mathbf{W}^2(\sigma,s) = r'\mathbf{W}'(\sigma',s') \qquad (22)$$

or

$$\begin{bmatrix} r^2(s^2 + \sigma s) & r^2(1 + s)(\sigma s)^{1/2} \\ r^2(1 + s)(\sigma s)^{1/2} & r^2(1 + \sigma s) \end{bmatrix} = \begin{bmatrix} r's' & r'(\sigma's')^{1/2} \\ r'(\sigma's')^{1/2} & r' \end{bmatrix} \qquad (23)$$

One can eliminate the r's by taking the ratios (letting w_{ij} represent the elements of $\mathbf{W}^2$)

$$\frac{w_{11}}{w_{22}} = \frac{w_{11}'}{w_{22}'} \qquad \frac{w_{12}}{w_{22}} = \frac{w_{12}'}{w_{22}'} \qquad (24)$$

giving

$$\frac{r^2(s^2 + \sigma s)}{r^2(1 + \sigma s)} = \frac{r's'}{r'} \qquad \frac{r^2(1 + s)(\sigma s)^{1/2}}{r^2(1 + \sigma s)} = \frac{r'(\sigma's')^{1/2}}{r'} \qquad (25)$$

One can then use the relation $w_{22} = w_{22}'$ to determine r'. One then has

$$s' = \left(\frac{s + \sigma}{1 + \sigma s}\right)s \qquad \sigma' = \frac{(1 + s)^2}{(1 + \sigma s)(s + \sigma)}\sigma \qquad (26)$$
$$r' = (1 + \sigma s)r^2$$

This is the result of Nelson and Fisher[6] for the nearest-neighbor Ising magnet translated into polypeptide language; the correspondence between the two models is outlined in the Appendix.

The fixed points of the renormalization group transformation are those points that remain unchanged by the transformation

$$(\sigma^*,s^*) = \mathbb{R}(\sigma^*,s^*) \qquad (27)$$

From eq 26 one sees that (0,1) and (0,0) are fixed points as well as the line $(1,s^*)$. In particular we note that at $s = 1$ one has the mapping

$$\sigma' = 4\sigma/(1 + \sigma)^2 \qquad (28)$$

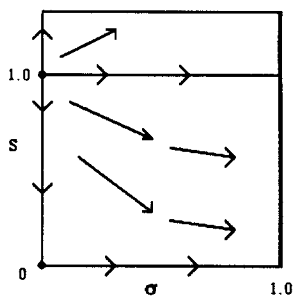

Figure 1. Renormalization group transformation flow pattern for the Zimm–Bragg model of the helix–coil transition in polyamino acids as given by eq 26. The solid dots indicate fixed points; the heavy line at $\sigma = 1.0$ is a line of fixed points. The general tendency is for points to move toward the $\sigma = 1$ line. The fixed point at (σ=0,s=1) corresponds to an infinitely sharp transition (step function) and is the analogue of the critical point at absolute zero for the 1-D Ising magnet.

The nature of the transformation of eq 26 is shown in Figure 1, where the flow of the transformation is schematically shown (the flow consists of discrete jumps, not continuous changes). One sees[6] that the point (σ=0,s=1) is a repelling fixed point; in the magnet this corresponds to a critical point at absolute zero. The main feature of the transformation is that $\sigma \rightarrow 1$, which has the physical interpretation of the model becoming less cooperative. Thus the renormalization group transformation can be viewed in this model as a process that successively turns the model into one of independent units, i.e.

$$Z \rightarrow (1 + s')^N \qquad (29)$$

Applying the secular equation method to the same model, one finds

$$(\lambda')^2 - (r')(1 + s')(\lambda') + (r')^2s'(1 - \sigma') = 0$$
$$(\lambda'')^2 - (r^2)(1 + 2\sigma s + s^2)(\lambda'') + (r^2)^2[(1 + \sigma s)(s^2 + \sigma s) - (1 + s)^2\sigma s] = 0 \qquad (30)$$

Taking the appropriate ratios to eliminate the r's, one finds

$$\frac{s'(1 - \sigma')}{(1 + s')^2} = \frac{(1 + \sigma s)(s^2 + \sigma s) - (1 + s^2)\sigma s}{(1 + 2\sigma s + s^2)^2} \qquad (31)$$

The problem is that this is the only equation one has. Since we have two parameters to determine, σ' and s', we cannot determine the complete mapping by this method. If we take the special case $s' = s = 1$, then eq 31 gives eq 28. If one had a 3 × 3 matrix for this model with a cubic secular equation, then one would have two equations in two unknowns and one could determine the complete mapping. This is the approach Li and Scheraga[1] took in their treatment of the helix–coil transition in polyamino acids; they used the Lifson–Roig model, which contains two parameters, the analogues of σ and s, but requires a 3 × 3 matrix. Since this is a slightly different model (in a minor way), Li and Scheraga do not obtain eq 26.

For the nearest-neighbor model the direct equivalence of the matrices proves to be the most useful technique; for more complicated models the secular equation method is easier to use (as long as one has the same number of equations and as one has parameters). Thus obtaining an exact renormalization group transformation requires a careful match of matrix size and number of parameters.

There is another way to obtain the same results derived from equating the coefficients of the two appropriate secular equations and that is to use the eigenvalues themselves. The renormalization group process requires that the partition function remain invariant to the renormalization group transformation, which results in the relations

Table I
Use of the Renormalization Group Transformation To Calculate the Free Energy[a]

n	partial sum	n	partial sum
0	0.0477	7	0.2694
1	0.1191	8	0.2721
3	0.1888	9	0.2734
4	0.2314	10	0.2741
5	0.2531	∞	0.2748
6	0.2639		

[a] Illustration of the use of eq 38 for the nearest-neighbor model with $s = 1$ and $\sigma = 0.1$. The entries are partial sums through the value of n indicated.

of eq 8. Using eq 14 to factor out the r's, one has the following ratio (where the r's are eliminated):

$$\frac{\lambda_i'(\sigma',s')}{\lambda_j(\sigma',s')} = \frac{\lambda_i(\sigma,s)}{\lambda_j(\sigma,s)} \tag{32}$$

One has $n - 1$ such equations that are independent. For the nearest-neighbor model that we are using as an example, there is then only one equation since $n = 2$ (as is the case with the secular equation method), and hence one cannot determine both σ' and s'. Taking the special case $s' = s = 1$, one has

$$\lambda_{i,1}' = 1 \pm \sigma'^{1/2} \qquad \lambda_{1,2}'' = (1 \pm \sigma^{1/2})^2 \tag{33}$$

giving

$$\frac{1 + \sigma'^{1/2}}{1 - \sigma'^{1/2}} = \frac{1 + \sigma + 2\sigma^{1/2}}{1 + \sigma - 2\sigma^{1/2}} \tag{34}$$

which on rearrangement gives eq 28 once again.

While the parameter r is an uninteresting parameter in that it simply rescales the zero of free energy and does not play an active role in the $(\sigma,s) \to (\sigma',s')$ map, it is not totally without interest since, as pointed out by Li and Scheraga,[1] it can be used to compute the free energy of the chain. If we let λ_n and r_n represent the nth generation or iteration of the renormalization group process, starting with $r_0 = 1$, then on the first iteration (assuming that N is large enough that we need consider only the largest eigenvalue)

$$Z = \lambda_0^N = (r_1\lambda_1)^{N/2} \tag{35}$$

or

$$\lambda_0 = (r_1\lambda_1)^{1/2} \tag{36}$$

If one keeps going in the renormalization group process one successively finds

$$\lambda_1 = (r_2\lambda_2)^{1/2} \qquad \lambda_2 = (r_3\lambda_3)^{1/2} \ldots \tag{37}$$

This gives for λ_0

$$\lambda_0 = r_1^{1/2} r_2^{1/4} r_3^{1/8} \ldots$$

or

$$\ln \lambda_0 = \sum_{n=1}^{\infty} (\ln r_n)/2^n \tag{38}$$

which gives the free energy per unit, $-RT \ln \lambda_0$. As an example, taking $s' = s = 1$ and $\sigma_0 = 0.1$, one finds from eq 33 that $\lambda_0 = 1 + \sigma^{1/2}$ and $\ln \lambda_0 = 0.2748$. Partial sums for eq 38 are shown in Table I; one sees that after 10 iterations one has $\ln \lambda_0$ to three figures. Thus the renormalization group equations (eq 26 in this example) can be viewed as an iterative algorithm to calculate the term $\sigma^{1/2}$ (an involved way to take a square root!).

One final tool of the renormalization group procedure will prove useful, and that is the behavior of the flow diagram in the neighborhood of the fixed points.[2] Near a fixed point, one can linearize the transformation (which in general is highly nonlinear, as illustrated by eq 26) near the fixed point (σ^*,s^*)

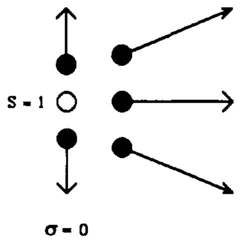

Figure 2. Nature of the flow pattern for the linearized renormalization group transformation for the model of Figure 1 in the neighborhood of the $(\sigma=0,s=1)$ critical fixed point. The flow is determined by eq 39 with the matrix of eq 41.

$$\begin{bmatrix} s' \\ \sigma' \end{bmatrix} = \begin{bmatrix} s^* \\ \sigma^* \end{bmatrix} + \mathbf{M}\begin{pmatrix} \Delta s \\ \Delta\sigma \end{pmatrix} \tag{39}$$

where $\mathbf{M}$ is the matrix of derivatives evaluated at (σ^*,s^*)

$$\mathbf{M} = \begin{bmatrix} (\partial s'/\partial s)^* & (\partial s'/\partial \sigma)^* \\ (\partial \sigma'/\partial s)^* & (\partial \sigma'/\partial \sigma)^* \end{bmatrix} \tag{40}$$

Using eq 26 as the critical fixed point $(\sigma^*=0,s^*=1)$, one finds[6]

$$\mathbf{M} = \begin{bmatrix} 2 & 0 \\ 0 & 4 \end{bmatrix} \tag{41}$$

Using eq 39 one can readily construct the nature of the flow pattern about (σ^*,s^*); this is shown in Figure 2 for the critical fixed point $(\sigma^*=0,s^*=1)$.

3. Polyethylene

Before considering the case of long-range interactions it is of interest to see how the renormalization group transformation works for a standard polymer like polyethylene. We use the following simple model.[10] Each unit can exist in three conformational states, trans, gauche$^+$ and gauche$^-$ (abbreviated t, g$^+$, g$^-$). We will take the trans state, the lowest energy state, as the zero of free energy. The Boltzmann factor for the gauche states is then designated as s

$$s = \exp(-\Delta\epsilon/RT) \tag{42}$$

where $\Delta\epsilon \approx +0.6$ kcal/mol (at room temperature one has $RT \approx 0.6$ kcal/mol and hence $s \approx 1/e \approx 1/3$). The combinations of successive conformational states g$^+$g$^-$ and g$^-$g$^+$ are strongly sterically unfavored (to all intents and purposes forbidden). We take σ to represent the Boltzmann factor reflecting this repulsive interaction

$$\sigma = \exp(-\Delta\epsilon^*/RT) \approx 0 \tag{43}$$

We first consider the case where $\sigma = 0$. When $\sigma = 0$ one cannot mix g$^+$ and g$^-$ states, and the polymer can be viewed as sequences of trans states alternating with either a sequence of all g$^+$ or all g$^-$ states:

$$\ldots\ t\ t\ t\ t\ g^+\ g^+\ t\ t\ t\ g^-\ g^-\ g^-\ t\ t\ t\ t\ t\ g^+\ t\ t\ g^+\ g^+\ t\ t\ t\ t\ \ldots \tag{44}$$

This can alternatively be viewed as simply the configuration

$$\ldots\ t\ t\ t\ t\ g\ g\ t\ t\ t\ g\ g\ g\ t\ t\ t\ t\ t\ g\ t\ t\ g\ g\ t\ t\ t\ t\ \ldots \tag{45}$$

where we understand that a sequence like g g g can be all g$^+$ or all g$^-$. The assignment of Boltzmann factors is then

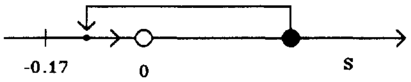

Figure 3. Renormalization group transformation flow pattern for the model for polyethylene given by eq 49. The model is the limiting case where g$^+$ and g$^-$ states are not allowed to mix. The transformation takes s from a positive (physical) value to a negative (nonphysical) value between the fixed point at $s = -0.1716$ and $s = 0$; successive transformations then take s toward the fixed point at $s = 0$.

given as shown below (each t state gets a factor 1; these are not shown)

$$\begin{array}{ccccccccccccccccccc} & & & & 2 & & & & & & & & & 2 & & & & & \\ \ldots & \mathrm{t} & \mathrm{t} & \mathrm{t} & \mathrm{g} & \mathrm{g} & \mathrm{g} & \mathrm{g} & \mathrm{t} & \mathrm{t} & \mathrm{t} & \mathrm{t} & \mathrm{t} & \mathrm{g} & \mathrm{g} & \mathrm{t} & \mathrm{t} & \mathrm{t} & \ldots \\ & & & & s & s & s & s & & & & & & s & s & & & & \end{array} \tag{46}$$

The factors of 2 are simple degeneracy factors since each g sequence can be either g$^+$ or g$^-$ (but not mixtures of the two). The transfer matrix that assigns the proper statistical weights is

$$\mathbf{W} = \begin{array}{c|cc} & \mathrm{t} & \mathrm{g} \\ \hline \mathrm{t} & 1 & 2 \\ \mathrm{g} & s & s \end{array} \tag{47}$$

Using the secular equation method one obtains

$$u_2 - (1 + s')u_1 - s'u_0 = 0$$
$$v_2 - (1 + 4s + s^2)v_1 + s^2v_0 = 0 \tag{48}$$

Taking the appropriate ratio of coefficients gives

$$\frac{s'}{(1 + s')^2} = \frac{-s^2}{(1 + 4s + s^2)^2} \tag{49}$$

Since the model is represented by a 2 × 2 matrix, one obtains only a single equation from the secular equations; since we have only one parameter in the model, s, this is sufficient (of course one has another equation to determine the "uninteresting" parameter r). To find the fixed points we set $s = s^*$ and we obtain the following polynomial from eq 49:

$$s(s^4 + 9s^3 + 20s^2 + 9s + 1) = 0 \tag{50}$$

which has the five roots $s^* = 0, -0.1716, -0.3820, -2.618$, and -5.828.

Since eq 49 is quadratic in s', given an initial value of s one will find two values of s'. Taking the smallest root, one finds the one-dimensional flow diagram shown in Figure 3. One sees that real positive values of s are transformed into negative values between the two fixed points $s^* = -0.1716$ and $s^* = 0$. The fixed point at $s^* = 0$ is attractive while that at $s^* = -0.1716$ is repulsive, successive transformations giving $s' \to 0$. Of course s' negative does not have any physical meaning (it corresponds mathematicaly to an imaginary temperature), and in this case the renormalization group transformation does not have any physical interpretation. Perhaps this is not surprising since there is no strong conformational transition in the original model: the only thing that happens on increasing the temperature is a slow increase in the population of gauche states (as T increases, $s \to 1$).

If we generalize the model to allow σ to be finite (but small), thus allowing some mixing of g$^+$ and g$^-$ states, one has the 3 × 3 transfer matrix

$$\mathbf{W} = \begin{array}{c|ccc} & \mathrm{g}^+ & \mathrm{t} & \mathrm{g}^- \\ \hline \mathrm{g}^+ & s & s & \sigma s \\ \mathrm{t} & 1 & 1 & 1 \\ \mathrm{g}^- & \sigma s & s & s \end{array} \tag{51}$$

The two secular equations are then

$$u_3 - (1 + 2s')u_2 + (s'^2 - (\sigma's')^2)u_1 + (s' - s'\sigma')^2u_0 = 0$$
$$v_3 - (1 + 4s + 2s^2 + 2\sigma^2s^2)v_2 +$$
$$[(2 + 4s)(s - \sigma s)^2 + (s^2 - \sigma^2s^2)^2]v_1 - (s - \sigma s)^4v_0 = 0 \tag{52}$$

The task of finding an explicit form for the renormalization group equations can be simplified by introducing the variables

$$x = s - \sigma s \qquad y = s + \sigma s \tag{53}$$

On taking the appropriate ratios of the coefficients one finds

$$(y')^3 + (ab/c)(y')^2 + (b^3/c)(y') + (b^3/c) = 0$$
$$x' = -y'(1 + y')/(ab/c + y')$$
$$r' = r^2(a/(1 + x' + y')) \tag{54}$$

where

$$a = 1 + 4x + 2x^2 + 2y^2$$
$$b = (2 + 4x)(x - y)^2 + (x^2 - y^2)^2$$
$$c = (x - y)^4 \tag{55}$$

Because of the cubic equation for y' in eq 54 one finds three sets of values for y', x', and r'. One observes that one always obtains $r = -1$ as one of the solutions. Exploring that case further, one finds the simplified renormalization group equations

$$s' = -(1 + 2s + s^2(1 + \sigma^2))$$
$$\sigma' = (1 - \delta)/(1 + \delta) \tag{56}$$

where

$$\delta = s^2(1 - \sigma)^2/[(2 + 4s) + s^2(1 + \sigma)^2] \tag{57}$$

Clearly $\sigma' = \sigma^* = 1$ is a fixed point with respect to σ. Using this value we find the fixed points for s by finding the roots of the equation

$$2s^2 + 3s + 1 = 0 \tag{58}$$

which has roots $s^* = -1/2, -1$. (It is of interest that $s^* = -1$ represents a pure imaginary temperature, i.e., $s^* = -1 = \exp(\pi i) = \exp(-\epsilon/RT)$ or $T = i(\epsilon/\pi R)$.) Thus the fixed points of the model are

$$(\sigma^*,s^*) = (1,-1/2), (1,-1) \tag{59}$$

The behavior in the neighborhood of the fixed points is described by the linearlized transformations through the matrix **M**

$$(\sigma^*{=}1,s^*{=}-1/2) \qquad \mathbf{M} = \begin{bmatrix} 0 & -1/2 \\ 0 & 0 \end{bmatrix}$$

$$(\sigma^*{=}1,s^*{=}-1) \qquad \mathbf{M} = \begin{bmatrix} 2 & -2 \\ 0 & 0 \end{bmatrix} \tag{60}$$

The flow behavior in the neighborhood of these points is shown in Figure 4. The large-scale flow pattern in the σ–s plane (for the $r' = -1$ solution) is that $\sigma' \to 1$ and $s' \to -\infty$. Again there is no simple physical interpretation that one can give to the renormalization group transformation in this case since the transformation requires negative (s) or imaginary (T) quantities.

There is another model that is mathematically quite similar to the polyethylene model. That case is a simple model for the binding of Mg^{2+} ions to DNA (single or double-stranded). The states "0" and "1" represent the states of the backbone phosphate groups with and without, respectively, a magnesium ion bound. The simplest model

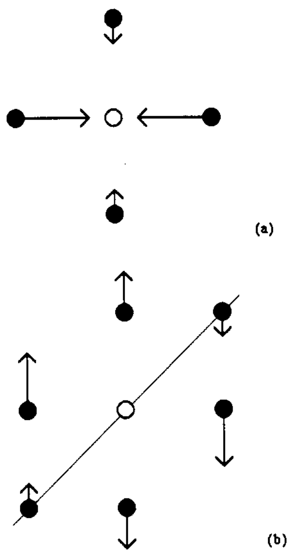

Figure 4. Flow pattern in the σ–s plane (oriented as in Figure 1) given by the linearized renormalization group transformation equations for the polyethylene model described by the transfer matrix of eq 51 (g^+ and g^- states are allowed to mix with a Boltzmann factor σ). The transformation is for the special case $r' = -1$; the fixed points are at (a) $\sigma = 1$, $s = -1/2$ and (b) $\sigma = 1$, $s = -1$. The matrices for the appropriate linearized equations are given in eq 60.

that fits the titration data[11] (titration with Mg^{2+}) is the simple requirement that (for charge or steric reasons) one cannot have neighboring bound magnesium ions. Thus a typical configuration of bound ions would be represented by

$$\ldots 0\,0\,0\,1\,0\,0\,0\,1\,0\,1\,0\,0\,0\,0\,1 \ldots \tag{61}$$

Letting

$$s = [\mathrm{Mg}^{2+}]K \tag{62}$$

where K is the binding constant for magnesium ions, the transfer matrix for this system is

$$\mathbf{W} = \begin{array}{c|cc} & 1 & 0 \\ \hline 1 & 0 & s \\ 0 & 1 & 1 \end{array} \tag{63}$$

The appropriate secular equations are

$$u_2 - u_1 - s'u_0 = 0$$

$$v_2 - (1 + 2s)v_1 + s^2 v_0 = 0 \tag{64}$$

giving

$$s' = -[s/(1 + 2s)]^2 \tag{65}$$

The fixed points are

$$s^* = 0, -1/4, -1 \tag{66}$$

The flow diagram is shown in Figure 5. One sees that starting from any real positive (physical) value of s, the first transformation gives s' between the fixed points $-1/4$ and 0 with s' then moving toward 0. This is similar to the behavior for the polyethylene model shown in Figure 3. Of purely mathematical interest is the behavior for $s < -1/4$. If we change variables as

$$x = (-1/4)s$$

then eq 65 becomes

$$x' = (1 - 2x)^2$$

The interval $-\infty$ to $-1/4$ in the variable s is then mapped onto the interval 0 to 1 in the variable x. The last equation represents a quadratic map $x \rightarrow x'$ which one finds represents chaotic motion.[12]

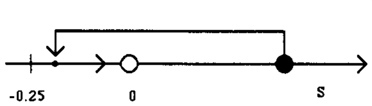

Figure 5. Renormalization group transformation flow pattern for the DNA/Mg^{2+} binding model of eq 63. The transformation maps positive (physical) values of s onto the negative axis between the fixed point $s = -1/4$ and $s = 0$. Successive transformations take s to the fixed point at the origin. For $s < -1/4$, the transformations are chaotic.

4. Long-Range Interactions

In this section we will treat a simple model for the helix-coil transition in DNA first introduced by Zimm.[13] We will first review the properties of the model and then treat it with the renormalization group method.

We have referred to the model we will discuss here as a simple one. That is because it does not take into account the specific-sequence nature of DNA. The heterogeneous nature of DNA is a very important ingredient in more realistic models for the unwinding of the DNA double helix and has been treated in detail elsewhere.[14] Here we will assume that the energetics of the double helix can be described by a parameter s that describes the average stability of the double helix. The model, introduced by Zimm,[13] is that illustrated in eq 3 where a run of 1's represents the double helix and a run of 0's represents a closed loop formed by breaking the hydrogen bonds holding the double helix together (unwinding from the ends, where one does not form a closed loop, will be treated later). The free energy of a closed loop formed from n base pairs is a nonexponential function of n; this means that we require a special factor σ_n for each loop size. The size dependence comes about from the fact that a loop has less entropy than a free chain. From the theory of random walks one finds the following form for σ_n as a function of n (the number of base pairs in a loop, or number of 0's in a sequence):

$$\sigma_n = \sigma/n^c \tag{67}$$

where σ is a nucleation parameter ($\sigma \ll 1$) and c is a characteristic exponent. For Gaussian chains in three dimensions one finds that $c = 3/2$ while for self-avoiding random walks one has[15] $c \cong 1.75$. In our numerical examples we will use $c = 3/2$ for simplicity.

The simplest way to obtain the partition function for very long chains is to use the function-generating technique of Lifson.[16] In that method the partition function is given by

$$Z(\sigma,s) = \lambda(\sigma,s)^N \tag{68}$$

where λ is the largest eigenvalue of the equation

$$U(\lambda)\ V(\lambda) = 1 \tag{69}$$

with the generating functions U and V defined as

$$U(\lambda) = \sum_{n=1}^{\infty} p_n/\lambda^n \qquad V(\lambda) = \sum_{n=1}^{\infty} q_n/\lambda^n \tag{70}$$

The quantities p_n and q_n are the statistical weights for sequences containing n 0's and n 1's, respectively. We have simply

$$p_n = \sigma_n = \sigma/n^c \qquad q_n = s^n \tag{71}$$

Equation 69 is the secular equation of the corresponding matrix for the same model, and λ is the largest eigenvalue. (One can obtain the secular equations for the models we have already discussed by using eq 69 with (nearest-neighbor polyamino acid model) $p_n = \sigma$, $q_n = s^n$; (polyethylene model, $\sigma = 0$ case) $p_n = 1$, $q_n = 2s^n$; and (Mg^{2+}

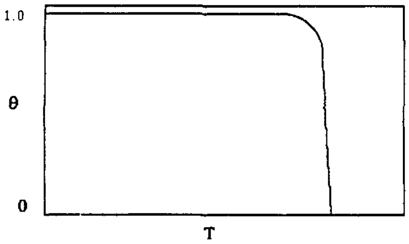

Figure 6. Schematic illustration of the helix–coil transition for DNA with long-range statistical weights for loops. The curve shows the fraction of helix, θ, as a function of temperature. $\theta \to 0$ exactly at a finite T_c; for $c = 3/2$ (the case shown), θ goes to zero with a finite slope.

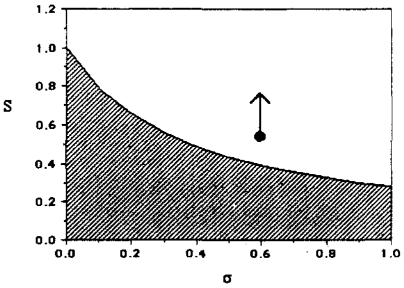

Figure 7. Locus $s_c(\sigma)$ for the DNA model giving the values of s_c at which $\theta \to 0$. The curve shown is for the case $c = 3/2$ (eq 73). For $s < s_c$ ($T > T_c$), the shaded area under the curve, $\theta = 0$ exactly and the system is in the pure random-coil state. The arrow shows the restricted renormalization group transformation discussed in section 5, where the transformation moves s away from the s_c locus toward larger values of s (lower T).

binding to DNA) $p_n = 1$, $q_1 = s$, and $q_n = 0$ for $n > 1$.

The fact that this model leads to a true phase transition in the infinite chain limit has been discussed by many workers.[15,17] A schematic curve showing θ, the fraction of double helix, as a function of temperature is shown in Figure 6. The simplest analytic result has been obtained by Fisher.[15] He showed that $\theta \to 0$ as $T \to T_c$ as follows:

$$\begin{aligned} \theta &\sim (T_c - T)^{\alpha} \qquad \alpha = (2 - c)/(c - 1) \\ &\sim (s - s_c)^{\alpha} \end{aligned} \tag{72}$$

For $c > 3/2$ the quantity θ goes to zero with an *infinite* slope while for $c < 3/2$ it goes to zero with a zero slope; θ has a finite slope at T_c for the special case $c = 3/2$. At T_c (or s_c) one finds that $\lambda_c = 1$; since this is the statistical weight for a chain unit in a free chain (we are taking the free chain as the zero of free energy), the physical nature of the transition is clear: above T_c the chain exists in the completely open form with absolutely no double helix present. Using eq 69, 70, and 71 with $\lambda_c = 1$, one finds

$$s_c = \frac{1}{1 + \sigma \sum_{n=1}^{\infty} (1/n^c)} = \frac{1}{1 + 2.612\sigma} \tag{73}$$

where we have used the value of the sum over $n^{-3/2}$ given by Truesdell.[18] Equation 73 gives a locus in the σ–s plane that divides the plane into two regions: for $s < s_c$ the system exists in the open-chain form only, while for $s > s_c$ there is some double helix in the system. This locus is shown in Figure 7; the hatched region is the open-chain only region ($s < s_c$). One expects the locus shown in Figure 7 to have special significance in the renormalization group method since it designates where the phase transition occurs. It is important to note that there is not a special critical value of σ for the phase transition. There will be a phase transition even if $\sigma = 1$ since the n^{-c} term makes the model highly cooperative. At T_c (s_c) the renormalization group transformation is trivial:

$$Z = 1^N = 1^{N/2} = \ldots \tag{74}$$

The question we would like to understand is how the system evolves toward this state.

In order to apply the renormalization group transformation to this model we need the matrix formulation of the partition function. Because of the long-range form of the σ_n we need a matrix that is $N \times N$ where N is the chain length (number of base pairs). The matrices required have been described in detail elsewhere.[8] For small N one has

$$\mathbf{W}_2 = \begin{bmatrix} a_1 & a_2 \\ 1 & 1 \end{bmatrix} \qquad \mathbf{W}_3 = \begin{bmatrix} a_1 & a_2 & a_3 \\ 1 & 0 & 0 \\ 0 & 1 & 1 \end{bmatrix}$$

$$\mathbf{W}_4 = \begin{bmatrix} a_1 & a_2 & a_3 & a_4 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 1 \end{bmatrix} \qquad \mathbf{W}_5 = \begin{bmatrix} a_1 & a_2 & a_3 & a_4 & a_5 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 1 \end{bmatrix} \tag{75}$$

where

$$a_1 = s; \quad a_n = s\sigma_{n-1}\ (n > 1); \quad a_N = s_{\mathrm{re}} \tag{76}$$

For a chain of N units one can have interior loops ranging in size from one unit to $N - 2$ units (to be a loop there must be at least one hydrogen-bonded base pair at each end); the factors a_2 through a_{N-1} assign statistical weights to these loops. The factor a_N represents states where there is run of 0's with a "1" state on the left border but not on the right border; hence a_N represents the case of an unzippered chain (nonloop state) on the right end of the molecule. Numerically one takes $s = s_{\mathrm{re}}$. The generalization to arbitrary N is obvious. The matrices $\mathbf{W}_N'$ are obtained simply be replacing the a_i with the primed variables a_i'. One finds that the matrices $\mathbf{W}_N^2$ have the form (illustrated for $N = 5$)

$$\mathbf{W}_5^2 = \begin{bmatrix} b_1 & b_2 & b_3 & b_4 & b_5 \\ a_1 & a_2 & a_3 & a_4 & a_5 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 1 & 1 \end{bmatrix} \tag{77}$$

where in general

$$b_i = a_1 a_i + a_{i+1} \qquad b_N = a_1 a_N + a_N \tag{78}$$

For $N = 2$–5 the explicit forms of the secular equations for $\mathbf{W}_N'$ and $\mathbf{W}_N^2$ are

$$\begin{gathered} u_2 - (1 + a_1')u_1 + (a_1' - a_2')u_0 = 0 \\ u_3 - (1 + a_1')u_2 + (a_1' - a_2')u_1 + (a_2' - a_3')u_0 = 0 \\ u_4 - (1 + a_1')u_3 + (a_1' - a_2')u_2 + (a_2' - a_3')u_1 + \\ (a_3' - a_4')u_0 = 0 \\ u_5 - (1 + a_1')u_4 + (a_1' - a_2')u_3 + (a_2' - a_3')u_2 + \\ (a_3' - a_4')u_1 + (a_4' - a_5')u_0 = 0 \\ v_2 - (1 + 2a_2 + a_1^2)v_1 + (a_1 - a_2)^2 v_0 = 0 \\ v_3 - (1 + 2a_2 + a_1^2)v_2 + (a_1^2 + 2a_2 + a_2^2 - 2a_1a_3 - \\ 2a_3)v_1 + (2a_2a_3 - a_2^2 - a_3^2 - (a_2 - a_3)^2)v_0 = 0 \\ v_4 - (1 + 2a_2 + a_1^2)v_3 + \\ (a_1^2 + 2a_2 + a_2^2 - 2a_1a_3 - 2a_4)v_2 + \\ (2a_1a_3 + 2a_2a_4 - a_2^2 - a_3^2 - 2a_1a_4)v_1 + (a_3 - a_4)^2 v_0 = 0 \\ v_5 - (1 + 2a_2 + a_1^2)v_4 + (a_1^2 + 2a_2 + \\ a_2^2 - 2a_1a_3 - 2a_4)v_3 + \\ (2a_1a_3 + 2a_2a_4 + 2a_4 - a_2^2 - a_3^2 - 2a_1a_5 - 2a_5)v_2 + \\ (2a_2a_5 + a_3^2 + a_4^2 - 2a_2a_4 - 2a_3a_5)v_1 - (a_4 - a_5)_2 v_0 = 0 \end{gathered} \tag{79}$$

To obtain explicit examples of the renormalization group transformation we set $a_N = 0$ and thus restrict the size of the loops that a molecule can contain. In this case all of the secular equations will be multiplied by a factor of $1 - \lambda$. Deleting this factor (we will discuss the physical significance of the $1 - \lambda$ factor shortly) one obtains the following reduced secular equations:

$$(N = 3) \quad -u_2 + a_1'u_1 + a_2'u_0 = 0$$
$$(N = 4) \quad -u_3 + a_1'u_2 + a_2'u_1 + a_3'u_0 = 0$$
$$(N = 5) \quad -u_4 + a_1'u_3 + a_2'u_2 + a_3'u_1 + a_4'u_0 = 0$$
$$(N = 3) \quad -v_2 + (a_1^2 + 2a_2)v_1 - a_2^2v_0 = 0$$
$$(N = 4) \quad -v_3 + (a_1^2 + 2a_2)v_2 + (2a_1a_3 - a_2^2)v_1 + a_3^2v_0 = 0$$
$$(N = 5) \quad -v_4 + (a_1^2 + 2a_2)v_3 + (2a_1a_3 + 2a_4 - a_2^2)v_2 + (a_3^2 - 2a_2a_4)v_1 - a_4^2v_0 = 0 \quad (80)$$

Taking the specific assignments

$$(N = 3) \quad a_1 = s, \quad a_2 = s\sigma, \quad a_3 = 0$$
$$(N = 4) \quad a_1 = s, \quad a_2 = s\sigma, \quad a_3 = s\sigma, \quad a_4 = 0$$
$$(N = 5) \quad a_1 = s, \quad a_2 = s\sigma_1, \quad a_3 = s\sigma_1, \quad a_4 = s\sigma_2, \quad a_5 = 0 \quad (81)$$

we obtain the following renormalization group transformation equations. For $N = 3$ we do not have enough equations to determine the transformation (one equation in two unknowns). For $N = 4$ and $N = 5$ one finds

$$(N = 4) \quad s' = (s^2 + 2s\sigma)(2/\sigma + 1)$$
$$\sigma' = (2 - \sigma)^2/(1 + 2\sigma/s) \quad (82)$$
$$(N = 5) \quad s' = (s^2 + \sigma_1 s)(2\sigma_1/\sigma_2 - 1)$$
$$\sigma_1' = (2\sigma_1/\sigma_2 - 1)(2\sigma_2 + 2\sigma_2/s - \sigma_1^2)$$
$$\sigma_2' = (2\sigma_1/\sigma_2 - 1)^2(\sigma_2 - 2\sigma_1\sigma_2)/(1 + 2\sigma_1/s) \quad (83)$$

The physical sense of these models is illustrated below (each 1 is assigned a factor s, not shown).

$$(N = 3) \qquad 1\;1\;1\;1\;\overset{\sigma}{0}\;1\;1\;\overset{\sigma}{0}\;1\;\overset{\sigma}{0}\;1\;1\;1\;\overset{\sigma}{0}\;1\;1$$

$$(N = 4) \qquad 1\;1\;\overset{\sigma}{0}\;0\;1\;1\;\overset{\sigma}{1}\;0\;1\;1\;\overset{\sigma}{0}\;0\;1\;\overset{\sigma}{1}\;0\;1$$

$$(N = 5) \quad 1\;1\;\overset{\sigma_1}{0}\;1\;1\;0\;\overset{\sigma_2}{0}\;0\;1\;1\;1\;1\;\overset{\sigma_2}{0}\;0\;1\;1\;\overset{\sigma_1}{0}\;1\;1\;1 \quad (84)$$

(In the general DNA model the largest chain size that one can treat with a given matrix is also the size of the matrix; here as a special case we restrict greatly the size of loops allowed.) Thus one is systematically introducing longer range interactions starting from the very restricted system of isolated 0's. Thus the above models and the nearest-neighbor model ($\sigma_n = \sigma$ for all n) represent two extremes, and one expects the behavior of the general DNA model to lie somewhere in between. The renormalization group transformation behavior of eq 82 and 83 is complicated. The general flow pattern for the $N = 4$ model is shown in Figure 8; the general tendency is for $s' \to \infty$ and $\sigma' \to 1$.

To find the secular equation for general N we define

$$\xi = \lambda'/r' \qquad \zeta = \lambda''/r^2 \quad (85)$$

One then forms the following determinants (letting **a** represent the vector of a_n values):

$$|\mathbf{W}_N'(\mathbf{a}') - \xi\mathbf{I}| = 0$$
$$|\mathbf{W}_N^2(\mathbf{a}) - \zeta\mathbf{I}| = 0 \quad (86)$$

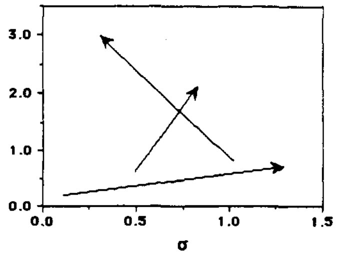

Figure 8. Renormalization group transformation flow pattern for the $N = 4$ model illustrated in eq 84, where only the sequences of zeros (1 0 1) and (1 0 0 1) are allowed, thus representing a greatly restricted version of the general DNA model. The transformation pattern is complicated with the general trend being toward $\sigma = 1$ and $s = \infty$; there tends to be an oscillation about the $\sigma = 1$ line as this limit is approached.

One finds (deleting a factor of $(-1)^N$ that multiplies the whole equation)

$$(1 - \xi)f_N + g_N = 0$$
$$(1 - \zeta)F_N + G_N = 0 \quad (87)$$

where

$$f_N = -\xi^{N-1} + \sum_{n=1}^{N-1} a_i'\xi^{N-n-1}$$
$$g_N = -a_N' \quad (88)$$

and

$$F_N = \sum_{i=1}^{N-1}\sum_{j=1}^{N-1} (-1)^j[\tfrac{1}{2}(1 - (-1)^{i+j})]\alpha_i\beta_j\zeta^{\eta_{ij}}$$
$$G_N = \sum_{k=1}^{N-1} (-1)^k(\alpha_k\beta_N - \alpha_N\beta_k)\zeta^{\nu_k} \quad (89)$$

with

$$\alpha_i = a_i, \quad \text{except } \alpha_2 = a_2 - \zeta$$
$$\beta_i = b_i, \quad \text{except } \beta_1 = b_1 - \zeta$$
$$\eta_{ij} = N - (i + j + 3)/2$$
$$\nu_k = |(N - 1 - k)/2| \quad (90)$$

The vertical lines in the expression for ν indicate that one is to take the integer part of the enclosed expression.

To obtain a working equation we note that we can simplify eq 87. For comparison we obtain

$$|\mathbf{W}(\mathbf{a}) - \lambda\mathbf{I}| = 0 \quad (91)$$

giving

$$(1 - \lambda)[-\lambda^{N-1} + \sum_{n=1}^{N-1} a_n\lambda^{N-n-1}] - a_N = 0 \quad (92)$$

First we note that if we eliminate unwinding from the right end by setting $a_N = 0$ we have

$$(1 - \lambda)\left(-\lambda + s\sigma\sum_{n=1}^{N-1}\frac{1}{n^c}\lambda^{-n}\right)\lambda^{N-2} = 0 \quad (93)$$

Deleting the λ^{N-2} factor and taking the limit $N \to \infty$, we can obtain this same equation from Lifson's generating function technique as follows. We form[18]

$$\frac{U_0(\lambda)}{1 - U(\lambda)\ V(\lambda)} = \infty \quad (94)$$

where now $U_0(\lambda)$ is the generating function for unwinding from the left end (we have eliminated unwinding from the right end by setting $a_N = 0$)

$$U_0(\lambda) = \sum_{n=0}^{\infty} \frac{1}{\lambda^n} = \frac{1}{\lambda - 1} \qquad (95)$$

where we use the statistical weight of unity independent of n for a free chain on the end of the molecule (we take a free chain as the zero of free energy). In the limit $N \rightarrow \infty$ eq 94 (setting the denominator equal to zero) and 93 are identical. Therefore we can identify the factor $1 - \lambda$ in eq 93 as the effect of the left end. Thus in eq 87 the g_N and G_N terms represent unwinding from the right end while the $1 - \xi$ and $1 - \zeta$ factors represent unwinding from the left end. Eliminating unwinding from both ends gives the simplified results

$$f_N(\xi) = 0 \qquad F_N(\zeta) = 0 \qquad (96)$$

Letting $N \rightarrow \infty$, one obtains our final working equations

$$\sum_{n=1}^{\infty} \left(\frac{r'}{\lambda'}\right)^n a_n' = 1$$

$$\sum_{n=1}^{\infty} \left(\frac{r^2}{\lambda''}\right)^n c_n = 1 \qquad (97)$$

where

$$c_1 = a_1^2 + 2a_2$$

$$c_n = (-1)^{n+1}a_n^2 + 2\left(a_{2n} + \sum_{k=1}^{n-1}(-1)^{k+1}a_k a_{2n-k}\right) \quad (n \geq 2) \qquad (98)$$

Taking the appropriate ratios to eliminate the r's, one has

$$\frac{a_n'}{(a_1')^n} = \frac{c_n}{(c_1)^n}$$

or

$$a_n' = (a_1')^n c_n/(c_1)^n \qquad (99)$$

This reduces the problem to the determination of two unknowns, a_1' and r'. Since one can calculate λ'' for the initial a_n parameters, one has the additional equation

$$\sum_{n=1}^{\infty} \left(\frac{r'}{\lambda''}\right)^n \left(\frac{a_1'}{c_1}\right)^n c_n = 1 \qquad (100)$$

which reduces the number of undetermined quantities to one.

We thus need one more condition to determine the renormalization group transformation for this model. In the original model one has

$$\lim_{n \to \infty} a_n/a_{n+1} = 1 \qquad (101)$$

Requiring the same limit for the a_n' variables gives

$$r' = 1 \qquad a_n' = c_n \quad (\text{all } n) \qquad (102)$$

We are thus led to the specific renormalization group equations

$$a_1' = a_1^2 + 2a_2$$

$$a_2' = -a_2^2 + 2(a_4 + a_1a_3)$$

$$a_3' = a_3^2 + 2(a_6 + a_1a_5 - a_2a_4)$$

$$a_4' = -a_4^2 + 2(a_8 + a_1a_7 - a_2a_6 + a_3a_5)$$

$$\text{etc.} \qquad (103)$$

There are two trivial fixed points for this transformation

$$a_n^* = 0 \ (\text{all } n) \qquad a_1^* = 1$$
$$a_n^* = 0 \ (\text{all } n > 1) \qquad (104)$$

or in terms of the variables s and σ_n

$$s^* = 0 \qquad s^* = 1$$
$$\sigma_n^* = 0 \ (\text{all } n) \qquad \sigma_n^* = 0 \ (\text{all } n) \qquad (105)$$

In the neighborhood of a fixed point, eq 103 give the following matrix **M** (the analogue of eq 40):

$$\mathbf{M} = 2\begin{bmatrix} a_1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \cdot \\ a_3 & -a_2 & a_1 & 1 & 0 & 0 & 0 & 0 & 0 & \cdot \\ a_5 & -a_4 & a_3 & -a_2 & a_1 & 1 & 0 & 0 & 0 & \cdot \\ a_7 & -a_6 & a_5 & -a_4 & a_3 & -a_2 & a_1 & 1 & 0 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & & \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{bmatrix} \qquad (106)$$

If one wants to describe the variation in s and the σ_n instead of a_n, one can use the relation

$$\begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \\ \cdot \\ \cdot \end{bmatrix} = \mathbf{B} \begin{bmatrix} s \\ \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \cdot \\ \cdot \end{bmatrix} \qquad (107)$$

where

$$\mathbf{B} = \begin{bmatrix} 1 & 0 & 0 & 0 & \cdot \\ 0 & s & 0 & 0 & \cdot \\ 0 & 0 & s & 0 & \cdot \\ 0 & 0 & 0 & s & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{bmatrix} \qquad (108)$$

One then has

$$\begin{bmatrix} s' \\ \sigma_1' \\ \sigma_2' \\ \sigma_3' \\ \cdot \\ \cdot \end{bmatrix} = \begin{bmatrix} s^* \\ \sigma_1^* \\ \sigma_2^* \\ \sigma_3^* \\ \cdot \\ \cdot \end{bmatrix} + \mathbf{C} \begin{bmatrix} \Delta s \\ \Delta\sigma_1 \\ \Delta\sigma_2 \\ \Delta\sigma_3 \\ \cdot \\ \cdot \end{bmatrix} \qquad (109)$$

where

$$\mathbf{C} = \mathbf{B}^{-1}\mathbf{M}\mathbf{B}$$

$$\mathbf{B}^{-1} = \begin{bmatrix} 1 & 0 & 0 & 0 & \cdot \\ 0 & s^{-1} & 0 & 0 & \cdot \\ 0 & 0 & s^{-1} & 0 & \cdot \\ 0 & 0 & 0 & s^{-1} & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{bmatrix} \qquad (110)$$

In the neighborhood of the fixed point ($s^*=1, \sigma_n=0$), one finds

$$\mathbf{C} = 2\begin{bmatrix} s & s & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \cdot \\ \sigma_2 & -s\sigma_1 & s & 1 & 0 & 0 & 0 & 0 & 0 & \cdot \\ \sigma_4 & -s\sigma_3 & s\sigma_2 & -s\sigma_1 & s & 1 & 0 & 0 & 0 & \cdot \\ \sigma_6 & -s\sigma_5 & s\sigma_4 & -s\sigma_3 & s\sigma_2 & -s\sigma_1 & s & 1 & 0 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{bmatrix} =$$

$$\begin{bmatrix} 2 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \cdot \\ 0 & 0 & 2 & 2 & 0 & 0 & 0 & 0 & 0 & \cdot \\ 0 & 0 & 0 & 0 & 2 & 2 & 0 & 0 & 0 & \cdot \\ 0 & 0 & 0 & 0 & 0 & 0 & 2 & 2 & 0 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{bmatrix} \qquad (111)$$

If one looks just in the s–σ_1 plane, as a first approximation, then one has

$$\begin{bmatrix} s' \\ \sigma_1' \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \end{bmatrix} + \begin{bmatrix} 2 & 2 \\ 0 & 0 \end{bmatrix} \begin{bmatrix} \Delta s \\ \Delta\sigma_1 \end{bmatrix} \qquad (112)$$

The flow pattern in the neighborhood of ($s^*=1, \sigma_n^*=0$) is shown in Figure 9. One sees that the approximate tendency is for the system to be repelled from the $s = 1$ line (as one moves away from the fixed point this would become the s_c line given by eq 73). This behavior is to be compared

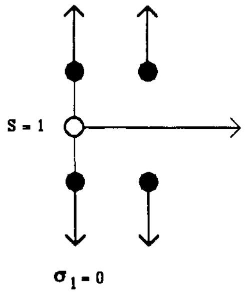

Figure 9. Flow pattern in the neighborhood of the (s=1,σ_n=0) fixed point in the s–σ_1 plane given by the linearized transformation equations for the DNA model (eq 112).

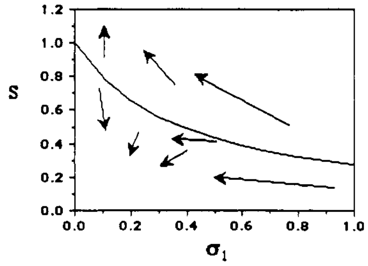

Figure 10. Renormalization group transformation flow pattern in the s–σ_1 plane for the DNA model using eq 103. The general tendency is for the transformation to move a point away from the $s_c(\sigma)$ locus, which is reproduced from Figure 7.

with the flow pattern for the nearest-neighbor model shown in Figure 2.

The general flow pattern using eq 103 is shown in Figure 10 where we show the behavior in the s–σ_1 plane. The critical line $s_c(\sigma)$ given by eq 73 is also shown for reference. One sees that the transformation moves away from the $s_c(\sigma)$ locus, moves generally toward the fixed point (s^*=1,σ_n^*=0), and then follows the pattern shown in Figure 9 for the behavior near that fixed point. The difference between the behavior of the DNA model and the 2-D Ising magnet is that there is no special critical value of σ (the analogue of the coupling constant K in the magnetic system—see the Appendix) but rather a line of phase transitions given by the locus $s_c(\sigma)$. The transformation moves the system roughly parallel to the $s_c(\sigma)$ line and is then swept away from the repelling fixed point at $s_c(\sigma{=}0) = 1$.

5. Discussion

In the previous section we presented a renormalization group treatment of a general model where each unit in a linear array can exist in one of two states, 0 and 1, and where sequences of one type (taken here as "0") had a general dependence of sequence statistical weight on sequence length, i.e.

$$(1\ 0\ 1) \rightarrow a_1 \quad (1\ 0\ 0\ 1) \rightarrow a_2 \quad (1\ 0\ 0\ 0\ 1) \rightarrow a_3 \quad \text{etc.} \tag{113}$$

While the model was suggested by DNA, where the a_n's are given by eq 71 and 76, the model is much more general than that specific system. The general secular equation for the model, in the limit of infinite N, is given by eq 92

$$(1-\lambda)\left(-\lambda + \sum_{n=1}^{\infty} \frac{a_n}{\lambda^n}\right) = 1 \tag{114}$$

As discussed elsewhere,[17] if the sum

$$\sum_{n=1}^{\infty} a_n \tag{115}$$

converges to a limit, the system will undergo a phase transition. The two largest eigenvalues are

$$\lambda_1 = 1 + \Delta(\mathbf{a}) \qquad \lambda_2 = 1 \tag{116}$$

The phase transition occurs when $\Delta(\mathbf{a}) \rightarrow 0$ and $\lambda_1 = \lambda_2 = 1$.

As seen in eq 103, the general renormalization group equations for this model involve an infinite set of coupled nonlinear equations in the a_n. If one wants a more restricted renormalization group treatment of the DNA model, one can use eq 116 to form the ratio of eigenvalues (see eq 8 and 32). This gives one a single equation in one unknown. For the DNA model, if one takes σ and c as fixed, this leaves s as a single variable, and one obtains the single variable mapping $s \rightarrow s'$. The use of restricted and more general renormalization group transformations was illustrated by the two models we treated for polyethylene. In the first model we took the special case $\sigma = 0$ and obtained a single equation for the mapping $s \rightarrow s'$. In the second model we let σ be a general variable and obtained the double mapping $\sigma \rightarrow \sigma'$ and $s \rightarrow s'$.

The basic equations for the restricted renormalization group treatment are (since $\lambda_2 = 1$, we drop the subscript on λ_1)

$$\lambda'(s') = \lambda^2(s)$$

or

$$\ln \lambda'(s') = 2 \ln \lambda(s) \tag{117}$$

From eq 116 we have two eigenvalues and can form the ratio equation (eq 32) to eliminate the r parameters. Since one of the eigenvalues is unity, this gives the same result as if one had only one eigenvalue and took the special case $r = r' = 1$ (which is the condition we found for the general renormalization group transformation in the last section). We define the following variables, which measure the distance from the transition temperature T_c:

$$\begin{aligned} \epsilon &= s - s_c \sim (T_c - T) \\ \epsilon' &= s' - s_c \sim (T_c - T') \end{aligned} \tag{118}$$

Then eq 117 reads

$$\ln \lambda'(\epsilon') = 2 \ln \lambda(\epsilon) \tag{119}$$

or using the form of a generalized homogeneous function[2]

$$\ln \lambda'(2^{\gamma}\epsilon) = 2 \ln \lambda(\epsilon) \tag{120}$$

which defines the exponent γ. From the work of Fisher[15] one has (where A is a constant)

$$\begin{aligned} \lambda(\epsilon) &= 1 + A[\epsilon]^{\mu} \\ \lambda'(\epsilon') &= 1 + A[\epsilon']^{\mu} \\ \mu &= 1/(c-1) \end{aligned} \tag{121}$$

Since the renormalization group requirement is that $\lambda'(\epsilon') = \lambda^2(\epsilon)$, one has for small ϵ

$$\epsilon' = (2^{1/\mu})\epsilon \tag{122}$$

From eq 120 one also has

$$\epsilon' = 2^{\gamma}\epsilon \tag{123}$$

and hence one obtains the characteristic exponent

$$\gamma = 1/\mu = c - 1 \tag{124}$$

We note that

$$\theta \sim \partial\lambda/\partial\epsilon \sim \epsilon^{\mu-1} \tag{125}$$

giving the result of eq 72.

From eq 122 one sees that $\epsilon' > \epsilon$ or $s' > s$, so that the restricted renormalization group mapping moves s away from the critical value of s_c; this is shown for a particular value of σ in Figure 7 (the behavior would be the same for all values of σ). Thus in the restricted renormalization group transformation (σ and c held fixed) the s_c line is a line of fixed points, the system moving away from the line under the renormalization group transformation. In the more general renormalization group transformation, where all of the a_n are allowed to vary (as in section 4), the renormalization group transformation moves the system parallel to the $s_c(\sigma)$ critical line toward the trivial fixed point ($s^*=1, \sigma_n^*=0$).

Appendix. Comparison of the 1-D Ising Ferromagnet with the Zimm-Bragg Model

In the one-dimensional Ising model for the ferromagnet the magnetic moment can exist in one of two orientations (states): with (+) or against (-) the external field. Nearest-neighbor-like spins (++ or --) are assigned a Boltzmann factor $\exp(K)$ while nearest-neighbor-unlike spins (+- or -+) are assigned a Boltzmann factor $\exp(-K)$; K is the coupling constant, $K = J/RT$. Another Boltzmann factor reflects the interaction of a spin with the external magnetic field: $\exp(L)$ for alignment with the external field and $\exp(-L)$ for alignment against the external field ($L = H/RT$, H being the magnetic field). The transfer matrix for this model is

$$\mathbf{W} = \begin{array}{c|cc} & + & - \\ \hline + & e^K e^L & e^{-K} \\ - & e^{-K} & e^K e^{-L} \end{array}$$

$$= e^K e^{-L} \begin{bmatrix} e^{2L} & e^{-2K} e^L \\ e^{-2K} e^L & 1 \end{bmatrix} \qquad \text{(A1)}$$

Comparing eq A1 with eq 20, one finds the following correspondence for the matrix elements:

$$s = e^{2L} \qquad \sigma = e^{-4K} \qquad \text{(A2)}$$

At zero external magnetic field ($L = 0$, the analogue of $s = 1$), the eigenvalues are

$$\lambda_{1,2} = e^K \pm e^{-K} \qquad \text{(A3)}$$

or

$$\lambda_1 = 2 \cosh K \qquad \lambda_2 = 2 \sinh K \qquad \text{(A4)}$$

Using the analogue of eq 32, one finds the renormalization group transformation $K \rightarrow K'$

$$\tanh K' = \tanh^2 K \qquad \text{(A5)}$$

where the flow is toward $K = 0$. If one lets $x = \exp(2K)$, then eq A5 can be written

$$x' = \tfrac{1}{2}(x + (1/x)) \qquad \text{(A6)}$$

which is to be compared with eq 28.

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Potentiometric Titration of Poly(vinylpyridines) and Hydrophobic Interaction in the Counterion Binding

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ABSTRACT: Potentiometric titrations of poly(4-vinylpyridine) (P4VP) and poly(2-vinylpyridine) (P2VP) were performed in the presence of 0.1 M NaCl or 0.1 M sodium benzenesulfonate (NaBS) in aqueous and 45 wt % aqueous ethanol solutions. It was found that pK_a values for P2VP titrated with benzenesulfonic acid (HBS) are higher at 40 and 25 °C and lower at 10 °C than those titrated with HCl at corresponding temperatures. The ΔH values for the protonation with HBS, which were estimated from the temperature dependence of the pK_a values of P2VP, become more endothermic at higher degrees of the polymer charge densities (α). In the case of P4VP, no significant difference was observed between HBS and HCl titrations. These results were discussed in terms of hydrophobic interactions between the polycations and BS$^-$ ions.

Introduction

Counterion bindings in aqueous polyelectrolyte solutions are largely influenced by the hydrations of relevant ions. Since most synthetic polyelectrolytes have hydrophobic main chains, hydration sheaths of the polyions are composed of ionic (and hydrogen bonding) hydrations around the charged (and polar) groups and of hydrophobic hydrations around the nonpolar moieties. When hydrophilic hydrations are predominant around the polyion, simple inorganic counterions such as alkali cations and halogen

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