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The one-dimensional $n \rightarrow 0$ vector model and the helix-coil transition

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The one-dimensional $n \rightarrow 0$ vector model is shown to be closely related to a model describing helix-coil transitions in polypeptides. This makes available a vast amount of theory developed in this area and allows a simple derivation of the self-avoiding walk length distribution corresponding to the one-dimensional $n \rightarrow 0$ vector model. The effect of the peculiar feature of this model, the extra factor $1/2$ for single site walks, is shown to be minor. The interpretation of the one-dimensional $n \rightarrow 0$ vector model as a model for helix-coil transitions commits little error and the corresponding "helix sequence" length distribution is in a first approximation identical to the helix sequence length distribution of existing models for the helix-coil transition. The equivalence between the $n \rightarrow 0$ vector model and an equilibrium polymerization model found by Wheeler *et al.* implies a close connection between the self-avoiding walk length distribution and the molecular weight distribution. Our results confirm the mean-field predictions that the molecular weights of the polymer species are distributed exponentially. The solution of the one-dimensional $n \rightarrow 0$ vector model shows a phase transition in the limit of zero magnetic field.

I. INTRODUCTION

The analogy found by de Gennes¹ and Des Cloizeaux² between a polymer system and a magnetic system has recently become the focus of extensive investigations. The connection between a simple self-avoiding walk and the n -component magnet in the limit $n \rightarrow 0$ ($n \rightarrow 0$ vector model) was first pointed out by de Gennes.¹ Des Cloizeaux² included a nonzero magnetic field and showed the equivalence between this model and a system of many mutually and self-avoiding walks of a broad length distribution. This polydispersity was first believed to be a serious limitation and the magnetic analogy appeared useful for qualitative purposes, like the determination of certain exponents, only. The situation changed, however, when Wheeler, Kennedy, and Pfeuty³ showed that the $n \rightarrow 0$ vector model in a very small magnetic field describes equilibrium polymerization. Their treatment was based on an earlier analysis by Sarma.⁴ Afterwards Wheeler and Pfeuty⁵ discovered an error in his analysis, which was also independently found by Gujrati,⁶ and argued that the corrected model is an even better model for equilibrium polymerization. Then Wheeler and Pfeuty^{7,8} went on to demonstrate the equivalence between a diluted $n \rightarrow 0$ vector model and equilibrium polymerization in solution. Finally Kennedy and Wheeler⁹ used the model for a description of the polymerization of living polymers. In all cases the correction mentioned before forced a different treatment of the first propagation step compared to the following ones. Although this could be rationalized for the various systems involved, its ultimate justification was that it made possible the correspondence with the magnetic model.

We will give the exact solution for the most simple case of the one dimensional $n \rightarrow 0$ vector model. In this limit the model is closely related to models for the helix-coil transitions in biopolymers.

The development of the theory describing these transitions mainly took place during the 1950's and 1960's and an extensive overview is given by Poland and Scheraga¹⁰ in their book devoted entirely to this subject. The general method taken is one where each polypeptide residue can exist in a helical state and a randomly coiled state. Furthermore, three consecutive residues have to be in a helical state before a hydrogen bond can be formed. Hence, to assign a statistical weight to a state of a residue, the state of the preceding two residues must be known. A simple but rather accurate description is given by the quadratic approximation to the "correct" model of Lifson and Roig.¹¹ The characteristic feature of this approximation is that the state of a residue depends only on the state of the nearest residue. Furthermore, all sequences of randomly coiled states and of helical states have the correct statistical weight except the single, isolated helical states. None of these models take helix sequences with less than the maximum number of hydrogen bonds into account. To allow for these states the Lifson-Roig¹¹ model will be slightly modified as will the quadratic approximation.

It will be shown that the one-dimensional $n \rightarrow 0$ vector model is closely related to the modified quadratic approximation. The correspondence is based on the identification of activated monomers, in the equilibrium polymerization interpretation of the $n \rightarrow 0$ vector model, and helical states. In fact, the interpretation of the $n \rightarrow 0$ vector model as a model for helix-coil transitions, while not entirely correct, commits little error. The calculated distribution function can be interpreted as a self-avoiding walk length distribution, a "helix sequence" length distribution or a "molecular weight" distribution. It is very broad and confirms the conclusions of the Tobolsky-Eisenberg¹² mean-field theory of equilibrium polymerization that the molecular weights of the polymeric species are distributed exponentially. As a "helix sequence" length distribution it is in first approximation identical to the "helix sequence" length distribution of the original quadratic approximation. Furthermore,

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the self-avoiding walk length distribution is to a very good approximation independent of the peculiar feature of the $n \rightarrow 0$ vector model, the presence of an extra factor $1/2$ for single site walks. An additional interesting feature emerging from the analogy between the one-dimensional $n \rightarrow 0$ vector model and the helix-coil transition is the prediction of a phase transition in the former in the limit of zero magnetic field. It corresponds directly to the fact that for an infinite chain the helix-coil transition becomes a genuine phase transition in the limit of a zero value for the cooperativity parameter σ . That the sharp transition in equilibrium polymerization systems has a similar mathematical basis as the helix coil transition in bipolymers was already pointed out by Tobolsky and MacKnight.¹⁵ The existence of a phase transition in the one-dimensional $n \rightarrow 0$ vector model is in agreement with a result of Balian and Toulouse.²⁷ They showed that analytic continuation on n , the number of components of the order parameter, yields phase transitions at finite temperatures for one-dimensional systems with short range forces, as soon as $n < 1$.

II. THEORETICAL MODELS

In this section the $n \rightarrow 0$ vector model, the Tobolsky-Eisenberg¹² model of equilibrium polymerization, and the model of Lifson and Roig¹¹ of helix-coil transitions will be introduced. The relation between the various models will be discussed.

The n -component vector model is a system of classical vector spins located on the lattice sites and interacting through the Hamiltonian

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j - m_0 H \sum_i S_i(1), \quad (2.1)$$

where the first summation is over all distinct nearest-neighbor pairs i and j . $\mathbf{S}$ is a classical n -component vector spin of magnetic moment m_0 and norm $\sqrt{n}$,

$$|\mathbf{S}|^2 = \sum_{\alpha=1}^n (S^{(\alpha)})^2 = n, \quad (2.2)$$

$S^{(1)}$ is the component of $\mathbf{S}$ parallel to the magnetic field H . The interesting feature of the $n \rightarrow 0$ limit is that all mean values of products of vector spins vanish except $\langle (S^{(\alpha)})^2 \rangle = 1$. In this limit the correct partition function corresponding to the above Hamiltonian is given by⁵

$$Z = \sum_{N_p} \sum_{N_b} \sum_{N_1} \tilde{J}^{N_b} (h')^{N_p} (1/2)^{N_1} \Gamma(N_p, N_b, N_1, N), \quad (2.3)$$

where $h' = m_0 H / kT$, $\tilde{J} = J/kT$ and $\Gamma(N_p, N_b, N_1, N)$ is the number of distinguishable ways of placing N_p mutually and self-avoiding walks containing N_b bonds on a lattice of N sites when N_1 of the walks are single site walks. The presence of an extra factor $1/2$ for these latter walks is a peculiarity of the model found by Wheeler and Pfeuty.⁵

In their general treatment of equilibrium polymerization Tobolsky and Eisenberg¹⁴ distinguished between three general cases. Our main interest is thermal polymerization. A prime example is given by the polymerization of sulfur.^{14,15} If m denotes a monomer and m^* an activated monomer the chemical equilibria are

given by

$$m \xrightleftharpoons{K_i} m^*, \quad (2.4)$$

$$(m^*)_{n-1} + m \xrightleftharpoons{K_{pn}} (m^*)_n, \quad (2.5)$$

where K_i and K_{pn} are equilibrium constants. The latter also contains contributions from the number of ways to arrange the chains on the lattice. To make this chain length dependence explicit, a constant K_p is introduced

$$K_p = \exp[-(\Delta H_p - T\Delta S_p)/RT], \quad (2.6)$$

where ΔH_p represents the change in enthalpy due to the activation of a monomer and its subsequent connection to the end of an already activated chain. ΔS_p represents the corresponding entropy contribution. Both ΔH_p and ΔS_p are supposed to be independent of chain length. The appropriate partition function for the equilibrium polymerization can now be written as

$$Y = \sum_{N_p} \sum_{N_b} \sum_{N_1} (2K_i)^{N_p} (K_p)^{N_b} (1/2)^{N_1} \Gamma(N_p, N_b, N_1, N), \quad (2.7)$$

where N_p , N_b , N_1 , and $\Gamma(N_p, N_b, N_1, N)$ are defined as before. The factor $1/2$, equivalent to taking the value of K_p for the first propagation step to be twice that for all others, is introduced to establish a correspondence with the $n \rightarrow 0$ vector model. In many cases it may be rationalized by observing that a newly activated monomer may be connected to either site of an activated monomer, not yet connected to any other monomer, at an adjacent lattice site. After one propagation step, however, only one site of the growing chain is available for a newly activated monomer. Specific examples can be found in Refs. 5 and 9. Comparing Eqs. (2.3) and (2.7) shows that both expressions are the same if the following identifications are made

$$\begin{aligned} K_p &= \tilde{J}, \\ 2K_i &= h'^2. \end{aligned} \quad (2.8)$$

The statistical weight v_j of a polymer of j monomers and prescribed conformation is

$$\begin{aligned} v_1 &= K_i, \\ v_j &= 2K_i (K_p)^{j-1}, \quad \text{if } j \geq 2. \end{aligned} \quad (2.9)$$

The characteristic feature of the α helix of a polypeptide is the hydrogen bond between the NH group of the i th residue and the CO group of the $(i+4)$ th residue. This is schematically illustrated in Fig. 1. The bonds connecting the two adjacent residues have a partial double bond character and are assumed to be fixed. The two other bonds of a residue have a partial freedom of rotation and the instantaneous value of the internal rotation angles determine whether we are dealing with a helical state or a randomly coiled state. Three consecutive units must be in the helical state before a hydrogen bond is formed. The maximum number of hydrogen bonds in a helix sequence of j units is $j-2$. A residue can therefore be in any of the three following states: A randomly coiled state, a helical state that does not contribute a hydrogen bond, and a helical state that contributes a hydrogen bond. Their statistical weights are taken to be 1 , $\sigma^{1/2}$ and s , respectively. This assignment

FIG. 1. Schematic representation of a polypeptide chain in the extended zig-zag conformation showing one hydrogen bond.

implies that the all coil state is taken as the reference state, just as the completely unreacted monomer system is taken as the reference state for the model of equilibrium polymerization introduced above. σ is very small, usually of the order 10^{-4} . The statistical weight v_j of a helix sequence of j units with $j-2$ hydrogen bonds according to this scheme, first introduced by Lifson and Roig,¹¹ is

$$\begin{aligned} v_1 &= \sigma^{1/2}, \\ v_j &= \sigma s^{j-2}, \quad \text{if } j \geq 2. \end{aligned} \quad (2.10)$$

In this case the statistical weight of a state of a residue depends on the state of the two preceding residues.

A very useful and rather accurate description is given by the quadratic approximation. The statistical weight v_j of a helix sequence of length j and $j-2$ hydrogen bonds is taken to be

$$\begin{aligned} v_1 &= \sigma/s, \\ v_j &= \sigma s^{j-2}, \quad \text{if } j \geq 2. \end{aligned} \quad (2.11)$$

According to this assignment the statistical weight of a state of a residue depends only on the state of the nearest residue. It is called a quadratic approximation because the secular equation for the eigenvalues of the transfer matrix is quadratic rather than cubic. A comparison with the correct assignment shows that all cases are treated correctly except the case $j=1$. The approximation involves making single isolated helical states more improbable and commits little error as long as their contribution to the free energy is small. Scheraga and Poland¹⁶ showed that this is true in the region of interest for the helix-coil transition.

To establish a correspondence between equilibrium polymerization and the helix-coil transition a monomer m is identified with a randomly coiled state, an activated monomer m^* with a helical state and a polymer of j units $(m^*)_j$ with a helix sequence of j units and $j-2$ hydrogen bonds. If we make the identification

$$\begin{aligned} K_1 &= \sigma/2s, \\ K_p &= s, \end{aligned} \quad (2.12)$$

then the statistical weight v_j of a helix sequence of j units and $j-2$ hydrogen bonds is

$$\begin{aligned} v_1 &= \sigma/2s, \\ v_j &= \sigma s^{j-2}, \quad \text{if } j \geq 2. \end{aligned} \quad (2.13)$$

Again all these cases are treated correctly except the case $j=1$. In this respect the $n \rightarrow 0$ vector model is equivalent to a model of helix-coil transition very simi-

lar to the quadratic approximation. There are differences between the two models that will be addressed in the next section. Furthermore, the extra factor $1/2$ for single site walks of the $n \rightarrow 0$ vector model results in the dependence of the statistical weight of the state of a residue on the state of the preceding two residues.

III. EXACT SOLUTIONS

A. Matrix method

The method generally used to evaluate the partition function of a classical lattice model and extensively applied to the models of helix-coil transitions,¹⁷⁻¹⁹ is the transfer matrix method. Upon diagonalizing of this matrix of conditional probabilities the partition function of a one-dimensional lattice of N sites becomes

$$Z(N) = \sum_{i=1}^k C_i \lambda_i^N, \quad (3.1)$$

where λ_i 's are the eigenvalues of the transfer matrix. In the case of nearest-neighbor interactions the number of eigenvalues k is equal to the number of different states of the quantity of interest. For a sufficiently large lattice the partition function can be approximated by

$$Z(N) \approx \lambda_1^N, \quad (3.2)$$

where λ_1 is the largest eigenvalue.

According to the theory of Lifson and Roig¹¹ the state of a residue of a polypeptide chain is determined exclusively by the instantaneous value of the internal rotational angles. Despite this clear definition, their model takes only helix sequences with the maximum possible number of hydrogen bonds (0 for a sequence of 1 or 2 helical states!) into account. We will modify their model in such a way that also all helix sequences with less than the maximum possible number of hydrogen bonds are allowed. The main reason for this modification is that we want to establish, as close as possible, an analogy between a model of the helix-coil transition and the $n \rightarrow 0$ vector model. To allow the above mentioned additional states of the polypeptide chain it will be assumed that a residue can be in three states: A randomly coiled state c , a helical state h , and a helical state h^* . The latter is defined as the first unit of any helix sequence, possibly of length 1, with a maximum possible number of hydrogen bonds. It is furthermore assumed that two adjacent residues cannot both be in the helical state h^* . In this way the state of a residue is uniquely defined. An example is given in Fig. 2(A).

The transfer matrix for the modified Lifson-Roig model is given by

	c	h	h^*	
c	1	0	$\sqrt{\sigma}$	
h	1	s	$\sqrt{\sigma}$	.
h^*	1	$\sqrt{\sigma}$	0	

(3.3)

The only difference between this matrix and the matrix of the original Lifson-Roig model¹¹ is the presence of $\sqrt{\sigma}$ instead of zero at the (2,3) position. It is not difficult to verify that this small change is just what is need-

FIG. 2. A. Schematic diagram of a portion of a polypeptide chain. Residues 2, 5, and 8 are the first units in a helical state of a helix sequence, with the maximum possible number of hydrogen bonds, of length 2, 3, and 1, respectively. a represents the only hydrogen bond, b represents a not yet formed hydrogen bond. B. Possible state of a portion of the equilibrium polymerization model. k , l , and n represent covalent bonds between two activated monomers. A and B correspond to each other under the correspondence given in the text.

ed to also take all helix sequences with less than the maximum possible number of hydrogen bonds into account. The equation for the eigenvalues becomes

$$\lambda(\lambda - 1)(\lambda - s) - \sigma + \sqrt{\sigma}(s - \lambda) + \sigma(1 - \lambda) = 0 \quad (3.4)$$

which differs from the equation of the Lifson-Roig model¹¹ by the additional term $\sigma(1 - \lambda)$. Further on it will be shown that in the region of interest $1 - \lambda$ is of the order $\sqrt{\sigma}$. In a first approximation both models will therefore give identical results.

The quadratic approximation amounts to replacing the statistical weight $\sqrt{\sigma}$ of a helix sequence of length 1 by σ/s [cf. Eqs. (2.10) and (2.11)]. The transfer matrix becomes

$$\begin{array}{c|ccc} & c & h & h^* \\ \hline c & 1 & 0 & \sigma/s \\ h & 1 & s & \sigma/s \\ h^* & 1 & s & 0 \end{array} \quad (3.5)$$

Again the only difference with the original quadratic approximation¹⁰ is the presence of σ/s at the (2, 3) position. As a consequence the secular equation is no longer quadratic which was the main motivation for its original introduction

$$\lambda(\lambda - 1)(\lambda - s) - \sigma\lambda + \frac{\sigma}{s}(s - \lambda) = 0. \quad (3.6)$$

A monomer of the equilibrium polymerization model can be in three different states: Not activated, activated but not contributing a propagation step (by definition the first activated monomer m^* of any polymer specy), and activated and also contributing a propagation step. To establish an analogy between this model and the above introduced model for helix-coil transitions [Eq. (3.5)] these different states will be identified with the three different states of a residue c , h , and h^* respectively. Figure 2 illustrates this identification.

The first model of equilibrium polymerization considered will be one for which all propagation steps are treated equally. The partition function for this model differs from Eq. (2.7) by the absence of the factors 2^{N_p} and $(1/2)^{N_1}$. The transfer matrix for this model, making the identification

$$\begin{aligned} K_t &= \sigma/s, \\ K_p &= s, \end{aligned} \quad (3.7)$$

becomes

$$\begin{array}{c|ccc} & c & h & h^* \\ \hline c & 1 & 0 & \sigma/s \\ h & 1 & s & \sigma/s \\ h^* & 1 & s & \sigma/s \end{array} \quad (3.8)$$

The only difference with the quadratic approximation of the modified Lifson-Roig model is the presence of σ/s instead of zero at the (3, 3) position. Consequently, the interpretation of this equilibrium polymerization model as a model to describe helix-coil transitions is not entirely correct. Certain different states of the equilibrium polymerization model do not, under the correspondence given, correspond to different states of a correct helix-coil model (Fig. 3). The error involved in such an interpretation is, however, minor since both transfer matrices [Eqs. (3.5) and (3.8)] lead to approximately the same distribution function, as will be shown in Sec. IV. The equation for the eigenvalues of this equilibrium polymerization model is

$$s(1 - \lambda)(s - \lambda) - \sigma\lambda = 0. \quad (3.9)$$

Finally the $n \rightarrow 0$ vector model will be considered. Using the identification given in Eq. (2.12) the transfer matrix takes the form

$$\begin{array}{c|ccc} & c & h & h^* \\ \hline c & 1 & 0 & \sigma/2s \\ h & 1 & s & \sigma/2s \\ h^* & 1 & 2s & \sigma/2s \end{array} \quad (3.10)$$

The interpretation of the $n \rightarrow 0$ vector model as a model for the helix-coil transition commits again a small error. At this point it should be emphasized that it is our aim to give the exact solution of the one-dimensional $n \rightarrow 0$ vector model and to explain certain striking similarities between this model and some of the models describing helix-coil transitions, rather than introducing an alternative model for the helix-coil transition. The equation for the eigenvalues of the one-dimensional $n \rightarrow 0$ vector model is

$$2s(1 - \lambda)(s - \lambda) - \sigma(\lambda + s) = 0. \quad (3.11)$$

Having obtained the exact solution the self-avoiding walk length distribution² will be derived next.

FIG. 3. Example of two different states of the equilibrium polymerization model that are also counted as two different states of the helix-coil model under the correspondence given in the text. In a correct helix-coil model only the first (A) would be present. k represents a covalent bond.

B. Sequence generating functions

Lifson²⁰ developed an alternative method of solving one-dimensional lattice models with nearest neighbor interaction. His method is particularly well suited for the calculation of certain distribution functions. Let u_j , v_j , and w_j denote the statistical weight of a sequence of j c units, j h units, and j h^* units, respectively. Define sequence generating functions by

$$U(\lambda) = \sum_{j=1}^{\infty} u_j \lambda^{-j}, \quad (3.12)$$

$$V(\lambda) = \sum_{j=1}^{\infty} v_j \lambda^{-j}, \quad (3.13)$$

$$W(\lambda) = \sum_{j=1}^{\infty} w_j \lambda^{-j}. \quad (3.14)$$

Then a matrix M is introduced, the columns of which represent the type of a specified sequence generating function and the rows represent the type of the preceding ones. Such a matrix takes the form

$$M = \begin{array}{c|ccc} & c & h & h^* \\ \hline c & 0 & V_1 & W_1 \\ h & U_1 & 0 & W_2 \\ h^* & U_2 & V_2 & 0 \end{array}. \quad (3.15)$$

The zeros on the diagonal are due to the requirement that no two adjacent sequences of the same type are allowed. The subscripts 1 and 2 refer to the fact that the expression for the sequence generating function may depend on the type of the preceding sequence generating function. In our case $U_1 = U_2 = U$ and $W_1 = W_2 = W$ but $V_2 \neq V_1 = 0$ because an h unit has to have an h^* as preceding unit. Lifson²⁰ showed that the largest eigenvalue of the transfer matrix λ_1 is also the largest root of the determinant equation

$$|1 - M(\lambda)| = 0, \quad (3.16)$$

where 1 stands for the unit matrix. In the last section the transfer matrix was chosen instead because it shows in a more striking way the similarities between the $n \rightarrow 0$ vector model and certain helix-coil transition models.

In our case $u_j = 1$ for all j and all models. Hence, $U(\lambda)$ is given by

$$U(\lambda) = (\lambda - 1)^{-1}, \quad (3.17)$$

Equation (3.16) can also be written as

$$\lambda = 1 + W(\lambda V + 1). \quad (3.18)$$

Due to this implicit expression for λ a simple expression for the distribution function of sequences of h units can be given. Following closely an argument first given by Poland and Scheraga²¹ for a somewhat simpler case we note first that the average number n_j of sequences of h units of length j is related to the partition function by

$$n_j = \frac{\partial \ln Z}{\partial \ln v_j} = N \frac{\partial \ln \lambda_1}{\partial \ln v_j}, \quad (3.19)$$

where λ_1 is the largest root of Eq. (3.18). The fraction f_j of sequences of h units having length j is given by

$$f_j = \frac{1}{\theta_h} \frac{v_j'}{\lambda_1} \frac{\partial \lambda_1}{\partial v_j}, \quad (3.20)$$

where θ_h is the total number of sequences of h units divided by the total number units N . From Eq. (3.18) it follows:

$$\frac{\partial \lambda_1}{\partial v_j} = \left\{ 1 - \frac{\partial W}{\partial \lambda_1} (\lambda_1 V + 1) - VW - \lambda_1 W \frac{\partial V}{\partial \lambda_1} \right\}^{-1} W \lambda_1^{1-j}. \quad (3.21)$$

Using the normalization condition $\sum_{j=1}^{\infty} f_j = 1$, Eq. (3.20) takes the simple form

$$f_j = (v_j' / \lambda_1^j) / \sum_{j=1}^{\infty} v_j' \lambda_1^{-j}. \quad (3.22)$$

The probability that an h -unit picked at random belongs to an h sequence of j units is

$$P_j = j f_j / \sum_{j=1}^{\infty} j f_j. \quad (3.23)$$

In the case of equilibrium polymerization P_j is the probability that a bond, connecting two activated monomers, picked at random belongs to a polymer of j such bonds or $j+1$ activated monomers. Combining the last two equations results in

$$P_j = j v_j' \lambda_1^{-j} / \sum_{j=1}^{\infty} j v_j' \lambda_1^{-j}. \quad (3.24)$$

IV. DISCUSSION

In order to derive the consequences of the exact results obtained so far, the eigenvalue λ_1 has to be evaluated for the various models. The emphasis will be on the quadratic approximation to the modified Lifson-Roig model [Eq. (3.5)], the equilibrium polymerization model with identical propagation steps [Eq. (3.8)], and the $n \rightarrow 0$ vector model [Eq. (3.10)]. We will restrict ourselves to the "transition" region, specifically $s = 1$. In this case the amount of polymerized material, or the fraction of helical units, is rather large and the differences between the models become minor. This follows immediately from the fact that for all three models to a first approximation the largest eigenvalue is given by

$$\lambda_1 \approx 1 + \sqrt{\sigma} + \dots \quad (4.1)$$

The differences between the λ_1 's is of the order σ which is very small for $\sigma \approx 10^{-4}$. The statistical weight v_j' for the first two mentioned models is

$$v_j' = s^j, \quad (4.2)$$

whereas for the $n \rightarrow 0$ vector model

$$v_j' = 2s^j. \quad (4.3)$$

In all cases

$$f_j = \frac{\lambda_1 - s}{s} (s/\lambda_1)^j \stackrel{s \approx 1}{\approx} \sqrt{\sigma} (1 + \sqrt{\sigma})^{-j}. \quad (4.4)$$

Similarly for the distribution function

$$P_j = \frac{(s - \lambda_1)^2}{s \lambda_1} j (s/\lambda_1)^j \stackrel{s \approx 1}{\approx} \frac{\sigma}{1 + \sqrt{\sigma}} j (1 + \sqrt{\sigma})^{-j}. \quad (4.5)$$

The maximum of the distribution function occurs for

$$j_{\max} = 1 / \ln \lambda_1 \stackrel{s \approx 1}{\approx} \sigma^{-1/2}. \quad (4.6)$$

The number and weight average lengths are given by

FIG. 4. Self-avoiding length distribution of the one-dimensional $n \rightarrow 0$ vector model for $h' = 10^{-2}$ and $\bar{J} = 1$ or equivalently $\sigma = 10^{-4}$ and $s = 1$.

$$L_n = \sum_{j=1}^{\infty} j f_j = \lambda_1 / (\lambda_1 - s) \approx 1 + \sigma^{-1/2}, \quad (4.7)$$

$$L_w = (\lambda_1 + s) / (\lambda_1 - s) \approx 1 + 2\sigma^{-1/2}. \quad (4.8)$$

Similar equations for helix sequence length distributions have been derived by Poland and Scheraga.²²

For the two equilibrium polymerization models P_j is simply the fraction of bonds belonging to polymers $(m^*)_{j+1}$. Because of the equivalence of a self-avoiding walk model and the $n \rightarrow 0$ vector model² it is also a self-avoiding walk length distribution. Figure 4 shows P_j as a function of j for $\sigma = 10^{-4}$. The distribution is very broad and confirms the conclusion of the Tobolsky-Eisenberg¹² mean field theory of equilibrium polymerization that the molecular weights of the polymeric species are distributed exponentially. Scott¹³ arrived at identical conclusions for equilibrium polymerization in solution. Moreover, Wheeler and Pfeuty^{5,8} showed the equivalence between these theories and the mean field approximation of the $n \rightarrow 0$ vector model and the diluted $n \rightarrow 0$ vector model, respectively. The persistence of the broad chain length distribution predicted by the mean-field theory is of some interest since the latter theory becomes exact only in the limit of infinite dimensionality.²³

The main difference between the two models of equilibrium polymerization is that, given identical initiation constants K_i and identical constants K_p , σ corresponding to the $n \rightarrow 0$ vector model [Eq. (2.12)] is twice as large as σ corresponding to the equilibrium polymerization model with identical propagation steps [Eq. (3.7)]. As a consequence the distribution of the latter is somewhat broader than that corresponding to the $n \rightarrow 0$ vector model. On the other hand, the self avoiding walk length distributions corresponding to the partition function Eq. (2.3) with and without the factor $(1/2)^{N-1}$ are in a first approximation identical for a given h' and $\bar{J}$.

In general one-dimensional systems with finite range interactions do not exhibit phase transitions. Kac *et al.*²⁴ and Fisher²⁵ showed that a phase transition can occur in a one-dimensional system when there are very long-range interactions or short-range interactions of

indefinitely great order. Fisher argued that the existence of a phase transition is determined by the unfavorable surface effects due to mixing of two kinds of states. If the unfavorable free energy becomes excessive, phase separation occurs. This is precisely what happens for the helix-coil transition in the limit $\sigma \rightarrow 0$.²⁶ Hence the one-dimensional $n \rightarrow 0$ vector model will also have a phase transition in the limit of zero magnetic field H . This is also obvious from the equation for the eigenvalues Eq. (3.11). For $\sigma = 0$, the largest eigenvalue is degenerate at $s = 1$. In this respect it is important to realize that it is not really the $n \rightarrow 0$ vector model that is solved but rather the model obtained by taking the thermodynamic limit of the $n \rightarrow 0$ limit of the finite n -component magnet. Wheeler and Pfeuty⁵ argued that this should be justified as long as H and $\bar{J}$ are sufficiently small. But, since $\bar{J}$ corresponds to s and since the phase transition occurs at $s = 1$, $\bar{J}$ is not small at all. On the other hand Balian and Toulouse²⁷ showed the existence of a phase transition in one-dimensional models with short-range interaction as soon as the number of components n of the order parameter is < 1 . This suggests that the interchange of the thermodynamic and the $n \rightarrow 0$ limit may ultimately be justified.

After this paper was submitted, a paper by Pfeuty and Wheeler²⁸ appeared also dealing extensively with the one-dimensional $n \rightarrow 0$ vector model. They showed that the interchange of the thermodynamic limit and the $n \rightarrow 0$ limit is permitted in this case. The connection between the one-dimensional $n \rightarrow 0$ vector model and the helix-coil transition was discussed using the Zimm-Bragg rather than the Lifson-Roig model. They did not address the self-avoiding walk length distribution, which is one of our main results. Reference 28 contains considerable material not discussed in the present manuscript.

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