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Equilibrium polymerization in one dimension: Exact solution by transfer matrix and renormalization group

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Equilibrium polymerization is very different in one dimension than in higher dimensionality. The transition that occurs in the limit of vanishing initiation equilibrium constant (which is a critical point in higher dimensionality) becomes a first-order transition at nonvanishing temperature in one dimension. A simple model of equilibrium polymerization that has been discussed recently for higher dimensionality is solved exactly by the transfer-matrix method in one dimension. The equivalent $n \to 0$ vector model of magnetism is also solved exactly for all fields and temperatures by transfer-matrix methods and is analyzed by an exact renormalization-group transformation. The renormalization-group analysis contains several interesting features including the fact that the parameter space of the Hamiltonian must be enlarged to six dimensions, yet remains finite. The connection of the model and transition treated here with the Zimm-Bragg model of the helix-coil transition and with the one-dimensional Ising model of magnetism is discussed.

I. INTRODUCTION

Equilibrium polymerization is a general phenomenon with examples in inorganic, organic, and biochemistry. Examples include the polymerization of liquid sulfur,[1] "living" organic polymers such as polytetrahydrofuran and poly-α-methylstyrene,[2] and the agglomeration of proteins such as actin and tubulin to form large supermolecular structures.[3] When the initiation step is restricted, either because of the small value of an initiation equilibrium constant K_1 for activation of monomers, as in the case in sulfur, or because of a small concentration of an initiator as can be the case with living polymers, the transition from monomer to polymer is quite sharp and exhibits features reminiscent of a thermodynamic phase transition.

Recently, we have argued[4] that equilibrium polymerization in these cases is a critical phenomenon that is closely analogous to the behavior of a ferromagnet near its Curie temperature in a very small magnetic field. We introduced a simple lattice model of equilibrium polymerization and showed that it is equivalent to the n-vector model of ferromagnetism in the formal mathematical limit $n \to 0$. The simple equilibrium-constant theory of Tobolsky and Eisenberg[5] is recovered as the mean-field approximation to the $n \to 0$ vector model.[6] The Tobolsky-Eisenberg (TE) theory expresses the properties of the system in terms of two equilibrium constants, $K_1 \ll 1$ for initiation and K_p' of order unity, for chain propagation. Our model[6] also expresses the properties in terms of two equilibrium constants K_1 (identical to TE's K_1) and K_p (proportional[7] to TE's K_p'). The polymerization transition is mathematically sharp only in the limit $K_1 \to 0$. For K_1 small but nonzero, the transition occurs over a small temperature range, but no mathematical singularity in the free-energy results. Incorporation of nonclassical critical behavior into the $n \to 0$ vector model through the use of renormalization group estimates for the critical exponents, and a simple scaling law equation of state results in an improved description of the transition in liquid sulfur[4] and in living polymers.[8] The critical effects depend upon the spatial dimensionality d. For sufficiently high dimensionality ($d \geq 4$) the (mean-field) Tobolsky-Eisenberg theory is adequate. Physical systems correspond to $d=3$ or even to $d<3$ for constrained geometries ($d=2$ for polymerization in a lamellar structure and $d=1$ for polymerization in a tube). Critical effects increase as the spatial dimensionality decreases. In the vicinity of the polymerization transition the fraction of monomer incorporated in polymer varies as

$$\left[\frac{K_p}{K_p^c}-1\right]^{1-\alpha}$$

and the specific heat diverges proportionally to

$$\left[\frac{K_p}{K_p^c}-1\right]^{-\alpha},$$

where α is predicted to be close to 0.23 in $d=3$ and 0.5 in $d=2$.[9]

In this paper we obtain the exact solution in one dimension of our model of equilibrium polymerization and show that the transition becomes "first order" in the sense that the fraction Φ of monomers incorporated in polymers increases discontinuously from zero to one as K_p' increases through $K_p'^{\,c}=1$, in the limit $K_1 \rightarrow 0$. On the other hand, the transition retains aspects of a critical point in that the free energy satisfies a scaling law equation of state in the variables K_1 and $K_p'-1$. The formal value of α becomes $\alpha=1$. As discussed in Sec. VI, this transition is not a violation of Landau's argument[10] for the nonexistence of phase transitions in one dimension.

We also obtain the exact solution in one dimension of the $n \rightarrow 0$ vector model of magnetism by an independent transfer-matrix calculation and verify the exact correspondence between the two models, derived earlier by a high-temperature expansion.[4,6] The scaling form of the free-energy and correlation functions is examined.

In addition, we carry out a renormalization-group analysis of the $n \rightarrow 0$ vector model in $d=1$ by an exact decimation transformation analogous to that employed for the Ising model by Nelson and Fisher.[11] Iteration of the transformation generates new coupling constants in addition to the spin coupling J and the field H. The parameter space of the Hamiltonian must be enlarged to six dimensions, but remains finite. The fixed points (actually surfaces) are identified and the critical exponents and the scaling form of the free energy are recovered. The exact solution of the one-dimensional $n \rightarrow 0$ vector model in this six-dimensional parameter space is obtained by transfer-matrix methods and is found to be in agreement with the values obtained from iterating the renormalization-group transformation.

The transition studied here is closely analogous to that in a one-dimensional Ising ferromagnet[12] in the limit $T \rightarrow 0$, where the magnetization jumps from -1 to $+1$ as H/kT varies from 0^- to 0^+, and this analogy can in fact be made precise by an exact mapping between the two problems in the limit $K_1 \rightarrow 0$. The transition is mathematically sharp only for $K_1=0$. For K_1 small but nonzero the transition is continuous but quite abrupt. It is then closely analogous to the helix-coil transition in proteins, studied by Zimm and Bragg,[13] and again a quantitative relationship exists. An outline of the paper is as follows. In Sec. II we define and solve the model of equilibrium polymerization, in Sec. III the exact solution of the $n \rightarrow 0$ vector model is obtained by transfer-matrix methods. Section IV contains the renormalization-group analysis and Sec. V the connection with other one-dimensional models. In Sec. VI we discuss our results and relate them to earlier work. We also present there a simple heuristic explanation of the very different behavior of polymerization in one dimension from that in $d>1$, and comment on the possibility of experimentally observing polymerization in one dimension.

II. MODEL AND EXACT SOLUTION

We consider a chain of N cells centered on the sites of a regular one-dimensional lattice, joined by $N-1$ lattice bond or edges. Each cell contains a monomer unit that can be in either of two states, active (A) or inactive (I). Two adjacent active monomers can be either bonded (b) or unbonded (u). Adjacent monomers can be bonded only if they are both active. Active monomers, either isolated or joined together by bonds, represent polymers (containing $1,2,\ldots,n \leq N$ sites). A statistical weight of 1 is associated with each inactive monomer while statistical weight $K_1 \ll 1$ is associated with each unbonded active monomer unit, and weight $(aK_1K_p^{n-1})$ is associated with each polymer of $n>1$ sites. The partition function for this chain of N monomer units can be written as

$$Z_N^c=\sum_{N_1,N_b,N_p}(aK_1)^{N_p}K_p^{N_b}a^{-N_1}\times\Gamma_N^{(c)}(N_1,N_b,N_p)\,, \tag{2.1}$$

where $\Gamma_N^{(c)}(N_1,N_b,N_p)$ is the number of ways to put N_p polymers, of which N_1 are one-cell polymers, on a lattice of N cells with a total of N_b bonds (the number of active monomers is N_p+N_b). Of course, the state of each monomer (A or I) can be associated with the underlying site of the lattice and the state of its potential bond with each neighbor (b or u) may be associated with the corresponding lattice bond or edge. For example, for a chain of $N=13$ lattice sites a configuration is shown in Fig. 1 with an associated statistical weight $(K_1^4K_p^3a^2)$.

This model corresponds to an equilibrium polymerization process with two distinct steps: initiation, governed by the statistical parameter K_1, and further growth, governed by K_p. The extra parameter a introduces a distinction between propagation of one-cell and larger polymers: aK_p for propagation of one-cell polymers, K_p for propagation of larger polymers. We have argued that $a=2$ is an appropriate choice for a ring-opening initiation process such as occurs in sulfur.[6] It is also appropriate in the case of certain living polymers.[8] We have also shown that $a=2$ results in an exact correspondence between Z_N^c in Eq. (2.1) and the partition function for the $n \to 0$ vector model on a lattice of N sites. Physically, K_p and K_1 are expected to depend on temperature through relations of the type

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

and

$$K_1 = \exp[(T\,\Delta S_1 - \Delta H_1)/RT] .$$

To calculate $Z_N^{(c)}$ exactly we first employ a recursion method similar to that employed by Zimm and Bragg.[13] We then introduce the conditional partition functions $Z_M^{(u)}$ and $Z_M^{(b)}$ which are partition functions for M sites with an edge added to the outside of the M'th site and specified to be (u) and (b), respectively. Then $Z_{M+1}^{(u)}$ and $Z_{M+1}^{(b)}$ can be expressed as linear combinations of $Z_M^{(u)}$ and $Z_M^{(b)}$

$$\begin{bmatrix} Z_{M+1}^{(u)} \\ Z_{M+1}^{(b)} \end{bmatrix} = \begin{bmatrix} 1+K_1 & (aK_1K_p)^{1/2} \\ (aK_1K_p)^{1/2} & K_p \end{bmatrix} \begin{bmatrix} Z_M^{(u)} \\ Z_M^{(b)} \end{bmatrix} . \tag{2.2}$$

To get (2.2) we observe that a site that is unbonded to either side can be either I or A and contributes a factor $1+K_1$ when added to the chain. We associate a weight $(aK_1K_p)^{1/2}$ to a site that forms either end of a chain, and a weight K_p with a site that is interior to a chain. This corresponds to assigning a factor $(aK_1)^{1/2}$ to each end of a chain and a factor $(K_p)^{1/2}$ to each of the sites at the end of a bond. The initial conditions are

$$Z_1^{(u)} = 1+K_1, \quad Z_1^{(b)} = (aK_1K_p)^{1/2} . \tag{2.3}$$

It follows from (2.2) and (2.3) that we can write

$$Z_N^{(c)} = Z_{M=N}^{(u)} = (1 \;\; 0)\underline{M}^N \begin{bmatrix} 1 \\ 0 \end{bmatrix} , \tag{2.4}$$

where

$$\underline{M} = \begin{bmatrix} 1+K_1 & (aK_1K_p)^{1/2} \\ (aK_1K_p)^{1/2} & K_p \end{bmatrix} . \tag{2.5}$$

This expression can be simplified by the standard procedure of expressing Z_N^c in terms of the eigenvalues and eigenvectors of the matrix $\underline{M}$. The secular equation is

$$\lambda^2 - \lambda(1+K_1+K_p) + K_p + K_1K_p(1-a) = 0 \tag{2.6}$$

giving eigenvalues

$$\lambda_0, \lambda_1 = \tfrac{1}{2}\{1+K_1+K_p \pm [(1+K_1-K_p)^2 + 4aK_1K_p]^{1/2}\} , \tag{2.7}$$

where λ_0 is the larger eigenvalue, corresponding to the plus sign, and λ_1 is the smaller, corresponding to the minus sign. The partition function can be expressed as

$$Z_N^c = \frac{\lambda_0^N(1+K_1-\lambda_1) + \lambda_1^N(\lambda_0-1-K_1)}{\lambda_0-\lambda_1} . \tag{2.8}$$

Equation (2.8) is valid for general N, both small and large. For any finite N, the limit $K_1 \to 0$ forces every monomer to remain inactive and, indeed, it is readily verified that $Z_N^c \to 1$ as $K_1 \to 0$. On the other hand, if we take the thermodynamic limit $N \to \infty$ for any nonzero K_1, we obtain for the limiting thermodynamic potential

$$f^{(c)}(K_1,K_p) \equiv \lim_{N\to\infty} N^{-1} \ln Z_N^c = \ln\lambda_0 \tag{2.9}$$

since $\lambda_0^N \gg \lambda_1^N$. This "free energy" exhibits a singularity at $K_1 = 0$, $K_p = 1$ corresponding to the abrupt phase change from all monomers inactive for $K_p < 1$ to all monomers active and bonded for $K_p > 1$:

$$\begin{aligned} &f = 0, \quad K_1 = 0, \quad K_p < 1 \\ &f = \ln K_p, \quad K_1 = 0, \quad K_p > 1 . \end{aligned} \tag{2.10}$$

It is convenient to define the concentrations of polymers and bonds as

$$x_p = \frac{\langle N_p \rangle}{N} = \left[\frac{\partial f}{\partial \ln K_1} \right]_{K_p} , \tag{2.11}$$

$$x_b = \frac{\langle N_b \rangle}{N} = \left[\frac{\partial f}{\partial \ln K_p} \right]_{K_1} . \tag{2.12}$$

The fraction of monomers incorporated in polymers (of length ≥ 1) is then

$$\Phi = x_p + x_b . \tag{2.13}$$

For $K_1 \to 0$, x_p is identically zero, but x_b and Φ change discontinuously from zero to unity as K_p increases through one. There is thus a first-order transition from an unpolymerized phase to a fully polymerized phase as K_p passes through one. This transition is analogous to the first-order transition in a ferromagnet below T_c, where the magnetization jumps from $-M$ to $+M$ as the magnetic field goes through zero from 0^- to 0^+. The point $K_p = 1$,

FIG. 1. A configuration of a chain of $N = 13$ lattice sites with a statistical weight $K_1^4 K_p^3 a^2$. Small dots correspond to lattice sites with inactive (I) monomers, the heavy dots correspond to active (A) monomers. Lines between heavy dots indicate bonded (b) adjacent monomers.

$K_1=0$ is analogous to $h=0$, $T<T_c$. In fact, as we show in Sec. V, there is an exact correspondence with a one-dimensional magnet where $T_c=0$ so that $K_1 \to 0$ corresponds to $T \to 0$ in the magnet. This transition is also closely related to the $d=1$ helix-coil transition,[13] where x_p represents the fraction of helix, as shown also in Sec. V.

When K_1 is nonzero but small, ϕ changes continuously but rapidly from $O(K_1)$ to $1-O(K_1)$ as K_p passes through one. This is illustrated in Fig. 2 where ϕ is shown as a function of K_p for K_1 equal to 10^{-6} and 10^{-12}.

The number concentration of polymers x_p also behaves very differently in $d=1$ than in higher dimensionality. According to both TE theory and our earlier scaling theory in three dimensions, x_p is predicted to vary proportionally to K_1 for $K_p<K_{pc}$ and proportionally to $K_1^{1/2}$ for $K_p>K_{pc}$. This behavior is verified by electron spin resonance (ESR) measurements[14] which are in good agreement with estimates of K_1 from bond energies and entropies above K_{pc}, and which indicate a precipitous drop in x_p near K_{pc}. In one dimension, however, x_p is predicted to vanish proportionally to K_1 for both $K_p>K_{pc}$ and $K_p<K_{pc}$. Only precisely at $K_p=K_{pc}=1$ does x_p vary proportionally to $K_1^{1/2}$ for small K_1. This behavior is illustrated in Fig. 3 which shows $\log_{10}x_p$ as a function of K_p for K_1 equal to 10^{-6} and 10^{-12}.

In the asymptotic limit of both K_1 and K_p-1 very small, the free energy in Eq. (2.9) can be expressed in the scaling form

$$f=(K_p-1)g_\pm\left[\frac{K_1}{|K_p-1|^2}\right], \tag{2.14}$$

where

$$g_\pm=\frac{1}{2}\left[1\pm\left[1+\frac{4aK_1}{(K_p-1)^2}\right]^{1/2}\right] \tag{2.15}$$

and the plus or minus sign is chosen according to whether (K_p-1) is positive or negative. [Terms of order $K_1/(K_p-1)$ have been neglected as necessarily small compared to those of order $K_1/(K_p-1)^2$ in the asymptotic limit.]

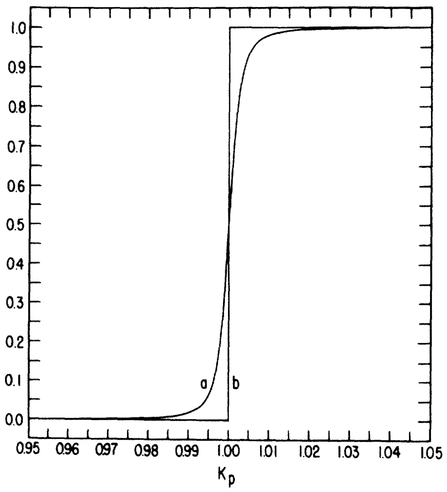

FIG. 2. Fraction of polymerized material ϕ as a function of temperature, measured by K_p. Curve a, $K_1=10^{-6}$; curve b, $K_1=10^{-12}$.

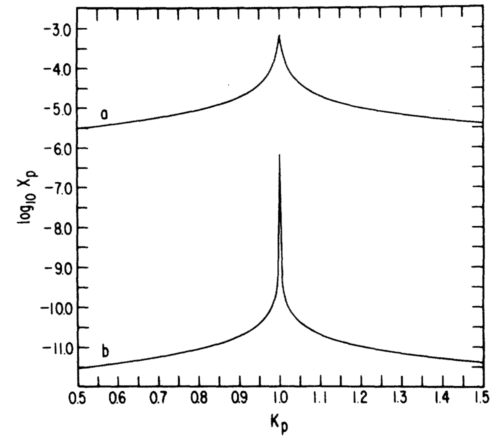

FIG. 3. Number concentration of polymers x_p as a function of K_p. Note logarithmic scale. Curve a, $K_1=10^{-6}$; curve b, $K_1=10^{-12}$.

By analogy with the behavior in higher dimensions we expect that $f \sim (K_p-1)^{2-\alpha}$, which leads to the exponent $\alpha=1$. In $d=1$, self-avoiding polymers are fully extended so that their mean length R varies linearly with the mean number of monomers per polymer P. The exponent ν defined by $R \sim P^\nu$ is thus $\nu=1$, and the hyperscaling relation $d\nu=2-\alpha$ is verified. For $a=2$ this identification of exponents can be justified by correspondence with the $n \to 0$ vector model, as discussed in Sec. III.

Equation (2.4) with (2.5) can also be obtained using the transfer-matrix idea. If the state of every edge (u or b) is specified, then the sum over states of every site can be performed in closed form and its contribution to that term in Z_N^c determined. If we make the identification of statistical weights as mentioned above, and append sites 0 and $N+1$ which are required to be in state I so that the bond joining them to the rest of the chain must be in state u, then Z_N^c can be expressed as a sum over the state of every bond, u or b, of a product of matrix elements joining adjacent bonds, and the result is Eq. (2.4) with (2.5).

Finally, it is useful in making the connection with the $n \to 0$ vector model, considered later, to note that if we associated the weight of a bond entirely with the site to its left, rather than dividing it evenly between the adjacent sites, then the partition function would take the distinct but equivalent form

$$Z_N^c = Z_{M=N}^{(u)} = (1\ \ 0)(\underline{M}')^N \begin{bmatrix} 1 \\ 0 \end{bmatrix} , \tag{2.16}$$

where

$$\underline{M}' = \begin{bmatrix} (1+K_1) & (aK_1)^{1/2} \\ (aK_1)^{1/2}K_p & K_p \end{bmatrix} \tag{2.17}$$

and

$$Z_1^{(u)} = 1+K_1,\ \ Z_1^{(b)} = (aK_1)^{1/2}K_p . \tag{2.18}$$

For completeness, we include here a brief treatment of the consequences of periodic boundary conditions on the correspondence between polymerization and the $n \to 0$ vector model. The conclusions are as follows. The limiting free energies $f = \ln\lambda_0$ are the same as for the open chain in each case without any manipulation of either model. However, for finite chains, the single term in the polymerization model partition function corresponding to a ring polymer of length N (i.e., every site active and every edge bonded) must be removed in order to retain the correspondence as an identity for all N. This is in keeping with the spirit of the correspondence between our polymerization model and the $n \to 0$ vector model in higher dimensions, namely, that no closed rings are allowed.[6] The term corresponding to the closed ring of size N is automatically excluded in the n-vector model by the limit $n \to 0$. The partition function for the polymerization model on a ring of N sites is most easily obtained by using the transfer-matrix interpretation mentioned above. For a ring, we need not add dummy sites 0 and $N+1$, but rather simply connect sites 1 and N with a lattice edge. Summing over the bond states of all bonds (and subtracting K_p^N for the ring state) then gives for the partition function on a ring

$$\begin{aligned} Z_N^{(r)}(K_p,K_1) &= \mathrm{Tr}\underline{M}^N - K_p^N \\ &= \lambda_0^N + \lambda_1^N - K_p^N , \end{aligned} \tag{2.19}$$

where λ_0 and λ_1 are the eigenvectors of $\underline{M}$ in Eq. (2.5) and are given by Eq. (2.7).

III. $n \to 0$ VECTOR MODEL, EXACT SOLUTION BY TRANSFER MATRIX

The n-vector model is a model introduced to describe various interacting systems and study their properties in the vicinity of a phase transition. It has been applied in particular to magnetic systems. To each site i of a chain of N sites we associate a vector $\vec{S}_i$ with n components S_i^α, $\alpha = 1,\ldots,n$, and with norm or length $n^{1/2}$. The energy is given by the Hamiltonian

$$\mathscr{H} = -H\sum_{i=1}^{N} S_i^1 - J\sum_{i=1}^{N-1} \vec{S}_i\cdot\vec{S}_{i+1} . \tag{3.1}$$

The partition function of the system is written

$$Z_N^c = \mathrm{Tr}\exp(-\beta\mathscr{H}) = \left\langle \exp\left[h\sum_{i=1}^{N} S_i^1 + \widetilde{J}\sum_{i=1}^{N-1} \vec{S}_i\cdot\vec{S}_{i+1} \right] \right\rangle_{(\vec{S}_1,\vec{S}_2,\ldots,\vec{S}_N)} , \tag{3.2}$$

where $\beta = 1/kT$, $h = \beta H$, and $\widetilde{J} = \beta J$, and where we have to take an angular average over all the possible orientations of the vectors $\vec{S}_1,\vec{S}_2,\ldots,\vec{S}_N$. The exponential can be expanded and averages of the form $\langle S_i^\alpha, S_j^\beta, \ldots, S_m^\gamma \rangle$ have to be done. In the limit $n \to 0$, as shown in previous papers in more detail[4,6] the only nonzero averages are of the form $\langle (S_i^\alpha)^2 \rangle = 1$, and Z_N^c can be written

$$Z_N^c = \sum_{N_1,N_b,N_p} (h^2)^{N_p}(\widetilde{J})^{N_b} 2^{-N_1} \Gamma_N^{(c)}(N_1,N_b,N_p) , \tag{3.3}$$

where $\Gamma_N^{(c)}(N_1,N_b,N_p)$ is the number of ways to put N_p polymers N_1 of which are one-site polymers on a chain of N sites with a total number of bonds N_b. This is identical to the partition function of the polymerization model introduced in Sec. II with the following relations between a, K_1, K_p, and h, $\widetilde{J}$:

$$a = 2,\ \ K_1 = \tfrac{1}{2}h^2,\ \ K_p = \widetilde{J} . \tag{3.4}$$

Exact solution by matrix method

The system being one-dimensional, we can calculate Z_N^c exactly for any N by averaging step by step, first over all orientations of $\vec{S}_1$, and then over $\vec{S}_2$, and so on up to $\vec{S}_N$. By integrating over $\vec{S}_1$ we get

$$\begin{aligned} Z_N^c &= \left\langle \langle \exp[hS_1^1 + \widetilde{J}\,\vec{S}_1\cdot\vec{S}_2] \rangle_{\vec{S}_1} \exp\left[h\sum_{i=2}^{N} S_i^1 + \widetilde{J}\sum_{i=2}^{N-1} \vec{S}_i\cdot\vec{S}_{i+1} \right] \right\rangle_{\vec{S}_2,\vec{S}_3,\cdots\vec{S}_N} \\ &= \left\langle (1 + \tfrac{1}{2}h^2 + h\widetilde{J}S_2^1) \exp\left[h\sum_{i=2}^{N} S_i^1 + \widetilde{J}\sum_{i=2}^{N-1} \vec{S}_i\cdot\vec{S}_{i+1} \right] \right\rangle_{\vec{S}_2,\ldots,\vec{S}_N} , \end{aligned} \tag{3.5}$$

where we have made use of the fact that, for $n\to 0$, only averages of $(S_i^{\alpha})^2$ and constants survive. After integrating over $\vec{S}_1,\vec{S}_2,\ldots,\vec{S}_p$, Z_N^c takes the general form

$$Z_N^c=\left\langle (A_p+B_pS_{p+1}^1)\exp\left[h\sum_{i=p+1}^{N}S_i^1+\tilde{J}\sum_{i=p+1}^{N-1}\vec{S}_i\cdot\vec{S}_{i+1}\right]\right\rangle_{\vec{S}_{p+1},\ldots,\vec{S}_N} . \tag{3.6}$$

The coefficients A_{p+1},B_{p+1} are linear functions of A_p,B_p. This can be written in the matrix form

$$\begin{bmatrix} A_{p+1} \\ B_{p+1} \end{bmatrix}=\underline{M}\begin{bmatrix} A_p \\ B_p \end{bmatrix} \tag{3.7}$$

with

$$\underline{M}=\begin{bmatrix} 1+\frac{1}{2}h^2 & h \\ h\tilde{J} & \tilde{J} \end{bmatrix} . \tag{3.8}$$

The initial conditions are

$$A_0=1,\ B_0=0 . \tag{3.9}$$

The last average, over S_N involves the exponential of only hS_N^1 and gives

$$A_{N-1}(1+h^2)+B_{N-1}h$$

which is of the form A_N, calculated from A_{N-1}, B_{N-1} using (3.7). It follows that we can write

$$Z_N^c=A_{p=N}=(1\ \ 0)\underline{M}^N\begin{bmatrix} 1 \\ 0 \end{bmatrix} , \tag{3.10}$$

where $\underline{M}$ is given by Eq. (3.8).

As before, this expression can be simplified by expressing Z_N^c in terms of the eigenvalues and eigenvectors of the matrix $\underline{M}$. The secular equation is

$$\lambda^2-\lambda(1+\tfrac{1}{2}h^2+\tilde{J})+\tilde{J}-\tfrac{1}{2}h^2\tilde{J}=0 , \tag{3.11}$$

which yields eigenvalues

$$\lambda_0,\lambda_1=\tfrac{1}{2}\{1+\tfrac{1}{2}h^2+\tilde{J}\pm[(1+\tfrac{1}{2}h^2-\tilde{J})^2+4\tilde{J}h^2]^{1/2}\} , \tag{3.12}$$

where λ_0 is the larger eigenvalue corresponding to the plus sign and λ_1 is the smaller, corresponding to the minus sign. The partition function can be expressed as

$$Z_N^c=\frac{\lambda_0^N(1+\frac{1}{2}h^2-\lambda_1)+\lambda_1^N(\lambda_0-1-\frac{1}{2}h^2)}{\lambda_0-\lambda_1} . \tag{3.13}$$

These results are identical to those obtained previously for the partition function of the polymerization model in Sec. II [Eqs. (2.4)—(2.8)] if $a=2$, and with $K_1=\frac{1}{2}h^2$ and $K_p=\tilde{J}$. This result confirms the correspondence between equilibrium polymerization and the $n\to 0$ vector model established through a high-temperature expression. The validity and usefulness of the correspondence between the two models has been previously demonstrated when we showed[6] that the approximate Tobolsky-Eisenberg theory of equilibrium polymerization[5] corresponds exactly to the mean-field theory of the $n\to 0$ vector model.

The thermodynamic potential

$$f^{(c)}=\lim_{N\to\infty}(N^{-1}\ln Z_N^c) \tag{3.14}$$

is given by

$$f^{(c)}(\tilde{J},h)=\ln(\tfrac{1}{2}\{(1+\tilde{J}+\tfrac{1}{2}h^2)+[(1-J+\tfrac{1}{2}h^2)^2+4\tilde{J}h^2]^{1/2}\}) . \tag{3.15}$$

Near $\tilde{J}=1$ and $h=0$ this has the scaling form

$$f^{(c)}=(\tilde{J}-1)g_{\pm}\left[\frac{h}{|J-1|}\right] , \tag{3.16}$$

where

$$g_{\pm}(x)=\tfrac{1}{2}[1\pm(1+4x^2)^{1/2}] . \tag{3.17}$$

This agrees with Eqs. (2.14)—(2.15) subject to identifications (3.4). With the usual definition of critical exponents for magnetic systems, we would expect the free energy to satisfy the scaling form

$$f(\tilde{J},h)=(\tilde{J}-\tilde{J}_c)^{2-\alpha}g_{\pm}\left[\frac{h}{|\tilde{J}-\tilde{J}_c|^{\beta\delta}}\right] , \tag{3.18}$$

which, with (3.16) and (3.17), implies

$$\alpha=1 ,$$
$$\beta\delta=1 . \tag{3.19}$$

The zero-field susceptibility is readily found to be

$$\chi(\tilde{J},h\to 0)=\left[\frac{\partial m}{\partial h}\right]_{\tilde{J}}=\left[\frac{1+\tilde{J}}{1-\tilde{J}}\right]\quad(\tilde{J}<1)$$
$$\chi(\tilde{J},h\to 0)=\left[\frac{2\tilde{J}}{\tilde{J}-1}\right]\quad(\tilde{J}>1) \tag{3.20}$$

from which it follows that $\gamma=1$. Applying the standard scaling relations we then obtain

$$\begin{aligned} &\alpha=\gamma=\beta\delta=1\ , \\ &\beta=2-\alpha-\gamma=0\ , \\ &\delta=\beta\delta/\beta=\infty\ , \\ &\nu=(2-\alpha)/d=1\ , \\ &\eta=2-\gamma/\nu=1\ , \end{aligned} \tag{3.21}$$

which agree with the earlier perturbative analysis by Balian and Toulouse.[15]

Despite the relatively straightforward identification of the critical exponents from the above quantities, there are aspects of the behavior of the $n\to 0$ vector model that are highly unusual. We have pointed out before[16] that if the free energy of the n-vector model is to satisfy both scaling, as in Eq. (3.18), and the requirement that $f(\tilde{J},h=0)$ is identically zero for $\tilde{J}<1$ [which Eq. (3.15) does satisfy], then the magnetic susceptibility must necessarily be negative for some values of $\tilde{J}$, h in the vicinity of the critical point whenever $\gamma>1$. Here $\gamma=1$ and this behavior is not required by our earlier argument. Nevertheless, it does occur. The magnetization and energy are given by

$$\begin{aligned} m &\equiv \left[\frac{\partial f}{\partial h}\right]_{\tilde{J}}=N^{-1}\left\langle\sum_i S_i^{(1)}\right\rangle \\ &=\frac{h\{1+(1+3\tilde{J}+\frac{1}{2}h^2)[(1-\tilde{J}+\frac{1}{2}h^2)^2+4\tilde{J}h^2]^{-1/2}\}}{1+\tilde{J}+\frac{1}{2}h^2+[(1-\tilde{J}+\frac{1}{2}h^2)^2+4\tilde{J}h^2]^{1/2}}\ , \end{aligned} \tag{3.22}$$

$$\begin{aligned} e &\equiv \left[\frac{\partial f}{\partial \tilde{J}}\right]_{h}=N^{-1}\left\langle\sum_i \vec{S}_i\cdot\vec{S}_{i+1}\right\rangle \\ &=\frac{1+(\tilde{J}-1+\frac{3}{2}h^2)[(1-\tilde{J}+\frac{1}{2}h^2)^2+4\tilde{J}h^2]^{-1/2}}{(\tilde{J}+1+\frac{1}{2}h^2)+[(1-\tilde{J}+\frac{1}{2}h^2)^2+4\tilde{J}h^2]^{1/2}}\ . \end{aligned} \tag{3.23}$$

This gives the somewhat bizarre result that

$$\lim_{h\to 0} m(\tilde{J},h)=0,\quad \tilde{J}\neq 1 \tag{3.24}$$

for both $\tilde{J}<1$ and $J>1$, but

$$\lim_{h\to 0} m(\tilde{J}=1,h)=\mathrm{sgn}(h)=\pm 1 \tag{3.25}$$

when $\tilde{J}=1$. The behavior of $m(\tilde{J},h)$ is sketched for several isochamps and isotherms in Figs. 4 and 5. As we have noted before,[16] the existence of negative values of $(\partial m/\partial h)_T$ for the $n\to 0$ vector model has no serious consequences for the physically relevant polymerization problem. Indeed, the concentration of polymers

$$x_p=\langle N_p\rangle/N=\tfrac{1}{2}hm$$

is an increasing function of $(2aK_1)^{1/2}=h$ for all values of $\tilde{J}=K_p$.

The behavior of $m(\tilde{J}=1,h)$ as $h\to 0$, given in Eq.

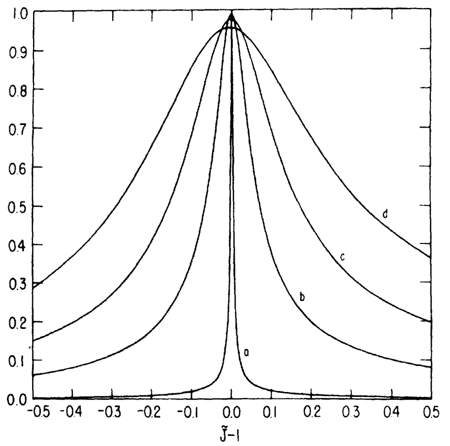

FIG. 4. Magnetization $m(\tilde{J},h)$ as a function of $\tilde{J}$ for various fields h. Curve a, $h=0.001$; b, $h=0.02$; c, $h=0.05$; d, $h=0.10$.

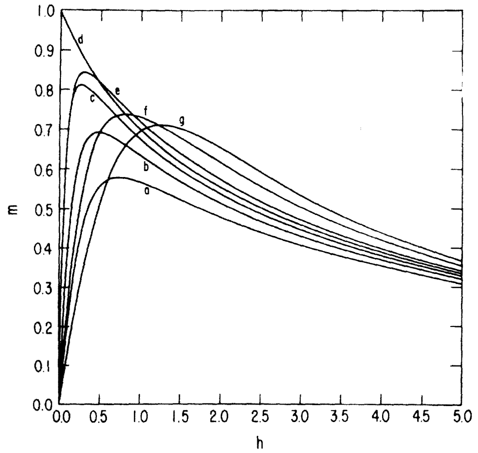

FIG. 5. Magnetization $m(J,h)$ as a function of h for various temperatures. Curve a, $\tilde{J}=2.0$; b, $\tilde{J}=1.5$; c, $J=1.2$. Curve d corresponds to $\tilde{J}=\tilde{J}_c=1.0$. Curve e, $\tilde{J}=0.8$; curve f, $\tilde{J}=0.4$; curve g, $\tilde{J}=0.1$.

(3.25), is in accord with the values of $\delta=\infty$ ascribed in Eq. (3.21). However, it should be noted that if instead one chose the definition

$$\lim_{h\to 0}\left[\frac{\partial m}{\partial h}\right]_T \sim h^{1/\delta-1}\ (\tilde{J}=1)\ , \tag{3.26}$$

then the behavior of m at $\tilde{J}=1$

$$m(\tilde{J}=1,h)=\mathrm{sgn}(h)(1-\tfrac{1}{2}\,|\,h\,|+\cdots) \tag{3.27}$$

would give the conclusion $\delta=1$. Similarly, since $m(\tilde{J},h=0)=0$ for $\tilde{J}>1$, no direct evaluation of the exponent β is possible.

Spin-correlation functions

The spin-correlation functions can also be calculated by standard transfer-matrix methods. For $i>j$, one finds

$$\langle S_i^1 S_j^1\rangle = \frac{(1\ \ 0)\underline{M}^{N-j}\underline{T}\,\underline{M}^{j-i-1}\underline{T}\,\underline{M}^{i-1}\begin{bmatrix}1\\0\end{bmatrix}}{(1\ \ 0)\underline{M}^{N}\begin{bmatrix}1\\0\end{bmatrix}}\ , \tag{3.28}$$

where $\underline{M}$ is given by Eq. (3.8) and where

$$\underline{T}=\begin{Bmatrix}h & 1\\ \tilde{J} & 0\end{Bmatrix}\,. \tag{3.29}$$

$\underline{T}$ is the matrix that expresses $A^{(i)}, B^{(i)}$ in terms of $A^{(i-1)}, B^{(i-1)}$, where

$$\langle (A^{(i-1)}+B^{(i-1)}S_i^1)S_i^1\exp(\tilde{J}\,\vec{S}_i\cdot\vec{S}_{i+1}+hS_i^1)\rangle_{\vec{S}_i} =(A^{(i)}+B^{(i)}S_{i+1}^1)\,. \tag{3.30}$$

Similarly, for the average $\langle S_i^1\rangle = m$ one finds

$$\langle S_i^1\rangle = \frac{(1\ \ 0)\underline{M}^{n-i}\underline{T}\,\underline{M}^{i-1}\begin{bmatrix}1\\0\end{bmatrix}}{(1\ \ 0)\underline{M}^{N}\begin{bmatrix}1\\0\end{bmatrix}}\,. \tag{3.31}$$

Applying the matrices $\underline{U}^R$ and $\underline{U}^L=(\underline{U}^R)^{-1}$ of left and right eigenvectors in (3.28) and (3.31) we obtain, for the spin-correlation function,

$$C(\,|\,j-i\,|\,)\equiv\langle S_i^1 S_j^1\rangle - \langle S_i^1\rangle\langle S_j^1\rangle\ , \tag{3.32}$$

the standard result ($j>i$)

$$C(\,|\,j-i\,|\,)=\tilde{T}_{12}\tilde{T}_{21}\lambda_0^{-2}\left[\frac{\lambda_1}{\lambda_0}\right]^{j-i-1}\ , \tag{3.33}$$

where

$$\underline{\tilde{T}}=\underline{U}^L\underline{T}\,\underline{U}^R\ , \tag{3.34}$$

near the critical point (3.33) can be written

$$C(\,|\,j-i\,|\,)\simeq\tilde{T}_{12}\tilde{T}_{21}\left[\frac{\lambda_1}{\lambda_0}\right]^{|j-i|} \tag{3.35}$$

from which we obtain the usual identification

$$\xi=\frac{-1}{\ln(\lambda_1/\lambda_0)}\ , \tag{3.36}$$

where ξ is the correlation length in units of the lattice spacing. The lack of any dependence upon $(j-i)$ except through $e^{-(j-i)/\xi}$ implies that $d-2+\eta=0$ or $\eta=1$, in agreement with the scaling result in Eq. (3.21). The dependence of λ_0 and λ_1 on $\tilde{J}$ when $h\to 0$ yields

$$\xi\sim\frac{1}{|\,1-\tilde{J}\,|}\quad (h=0,\tilde{J}\simeq 1) \tag{3.37}$$

from which follows $\nu=1$, again in agreement with (3.21).

The zero-field spin-correlation function can be calculated from (3.33) for all values of $\tilde{J}$ by taking the limit $h\to 0$. It is found to be, for $|\,j-i\,|>0$,

$$\begin{aligned}C(\,|\,j-i\,|\,)&=\tilde{J}^{|j-i|}\quad(\tilde{J}<1)\\&=\tilde{J}^{-|j-i|}\quad(\tilde{J}>1)\\&=0\quad(\tilde{J}=1)\,.\end{aligned} \tag{3.38}$$

The last result can be refined by retaining the lowest-order terms in h. The result is, for $h\gtrsim 0$ and $|\,j-i\,|>0$,

$$C(\,|\,j-i\,|\,)\simeq(\tfrac{1}{2}h)^2\left[\frac{1-h}{1+h}\right]^{|j-i|}\,. \tag{3.39}$$

The magnetic susceptibility and spin-correlation functions are related by the fluctuation relation

$$\begin{aligned}\left[\frac{\partial m}{\partial h}\right]_T&=\lim_{N\to\infty}N^{-1}\sum_{i=1}^{N}\sum_{j=1}^{N}(\langle S_i^1S_j^1\rangle-\langle S_i^1\rangle\langle S_j^1\rangle)\\&=\langle(S_i^1-\langle S_i^1\rangle)^2\rangle+2\sum_{j=1}^{\infty}(\langle S_i^1S_{i+j}^1\rangle\\&\qquad-\langle S_i^1\rangle\langle S_{i+j}^1\rangle)\ ,\end{aligned} \tag{3.40}$$

where, in the second line, i is a "typical" interior spin, infinitely distantly removed from the ends of the (infinite) chain. For both $\tilde{J}>1$ and $\tilde{J}<1$, the average $\langle S_i^1\rangle$ is zero for $h=0$. For $\tilde{J}<1$, it is easily established that $\langle (S_i^1)^2\rangle=1$ for $h=0$, so that the thermodynamic average of $(S_i^1)^2$ is identical with its angular average. For $\tilde{J}>1$, however, one finds that, for a spin j sites removed from the end of the chain,

$$\langle (S_j^1)^2\rangle=\tilde{J}^{-j}\quad(h=0) \tag{3.41}$$

so that, for a spin in the interior of an infinite chain,

$$\langle (S_i^1)^2 \rangle = 0 \quad (\tilde{J} > 1, h = 0) \,. \tag{3.42}$$

Using these results, we easily verify the fluctuation relation (3.40) both above and below T_c [cf. Eq. (3.20)]:

$$\begin{aligned} \left[\frac{\partial m}{\partial h} \right]_T &= 1 + 2 \sum_{j=1}^{\infty} \tilde{J}^j = \frac{1+\tilde{J}}{1-\tilde{J}} \quad (\tilde{J} < 1) \\ &= 2 \sum_{j=1}^{\infty} \tilde{J}^{-j} = \frac{2\tilde{J}}{\tilde{J}-1} \quad (\tilde{J} > 1) \,. \end{aligned} \tag{3.43}$$

When $\tilde{J}$ is exactly one, the $h \to 0$ limit of $\langle (S_i^1)^2 \rangle$ is $\frac{1}{2}$ for a spin far removed from the end of the chain so that

$$\langle (S_i^1)^2 \rangle - m^2 = -\tfrac{1}{2} \,.$$

With Eq. (3.39), this gives for the zero-field limit of the susceptibility at T_c,

$$\lim_{h \to 0} \left[-\tfrac{1}{2} + 2 \sum_{j=1}^{\infty} (\tfrac{1}{2} h)^2 \left[\frac{1-h}{1+h} \right]^j \right] = -\tfrac{1}{2}, \tag{3.44}$$

in agreement with (3.27). Thus, the value $-\frac{1}{2}$ for the zero-field limit of the susceptibility at T_c is due entirely to the $(j-i)=0$ term in the correlation function and is not related to the divergence of the correlation length at all.

The analysis of the scaling form of the correlation functions is facilitated by the transformation to the parametric variables r and θ defined by

$$\begin{aligned} 2h &= r \sin\theta \,, \\ 1 - \tilde{J} &= r \cos\theta \,. \end{aligned} \tag{3.45}$$

In these terms, and to first order in r, the matrices $\underline{M}$ and $\underline{T}$ can be written as

$$\underline{M} = \begin{bmatrix} 1 & \frac{1}{2} r \sin\theta \\ \frac{1}{2} r \sin\theta & 1 - r\cos\theta \end{bmatrix} \tag{3.46}$$

and

$$\underline{T} = \begin{bmatrix} \frac{1}{2} r \sin\theta & 1 \\ 1 - r\cos\theta & 0 \end{bmatrix} . \tag{3.47}$$

The matrix of normalized eigenvectors of $\underline{M}$ is, to the same order,

$$\underline{U}^R = \begin{bmatrix} \cos(\theta/2) & -\sin(\theta/2) \\ \sin(\theta/2) & \cos(\theta/2) \end{bmatrix} = (\underline{U}^L)^T \tag{3.48}$$

and the eigenvalues are readily found to be expressible in the form

$$\begin{aligned} \lambda_0 &= 1 + r \sin^2(\theta/2) \,, \\ \lambda_1 &= 1 - r \cos^2(\theta/2) \,. \end{aligned} \tag{3.49}$$

This gives, for the thermodynamic potential (to lowest order in r),

$$f = \ln\lambda_0 \simeq r \sin^2(\theta/2) \,, \tag{3.50}$$

which, with (3.45), is precisely equivalent to (3.16) with (3.17). For the magnetization m we have, either by differentiating (3.50) or from (3.22),

$$m = \sin\theta + O(r) \,, \tag{3.51}$$

in agreement with the assignment $\beta = 0$ in (3.21).

Similarly, for the susceptibility, one obtains

$$\left[\frac{\partial m}{\partial h} \right]_{\tilde{J}} = \frac{2\cos^2\theta}{r} + O(1) \,, \tag{3.52}$$

in agreement with the identification $\gamma = 1$ in (3.22). Thus, the scaling part of the susceptibility is nonnegative, but vanishes on the line $\cos\theta = 0$, corresponding to $\tilde{J} - 1$. It is the smooth background term and higher-order terms in r that are responsible for the negative susceptibility near $T - T_c$.

For the correlation length we obtain

$$\xi = r^{-1}[1 + O(r)] \tag{3.53}$$

and, for the spin-correlation function, to lowest order in r and for $|j-i| > 0$,

$$C(|j-i|) \simeq \cos^2\theta \exp(-|j-i|/\xi) \,. \tag{3.54}$$

The sum of $C(|j-i|)$ over i and j gives as the dominant scaling part of the susceptibility

$$\frac{1}{N} \sum_{i,j=1}^{N} C(|j-i|) \sim \frac{2\cos^2\theta}{r} \tag{3.55}$$

in agreement with (3.52).

It is also possible to calculate the transverse correlation functions

$$C^\alpha(|j-i|) = \langle S_i^\alpha S_m^\alpha \rangle - \langle S_i^\alpha \rangle \langle S_j^\alpha \rangle \tag{3.56}$$

for $\alpha \neq 1$. The procedure is analogous to that described above except that the term S_i^α as well as S_i^1 and 1 must be kept track of, with the result that $\underline{M}$ and $\underline{T}$ and therefore $\underline{U}^R$ and $\underline{U}^L$ must be augmented to 3×3 matrices. The result is that, for $j \neq i$ and $\alpha \neq 1$,

$$\begin{aligned} C^\alpha(|j-i|) &\sim \tilde{J}^{|j-i|} \quad (\tilde{J} < 1, h \to 0) \\ &\sim O(h^2) \quad (\tilde{J} > 1, h \to 0) \\ &\sim \tfrac{1}{2} \left[\frac{1}{1+h} \right]^{|j-i|} \quad (\tilde{J} = 1, h \to 0) \,. \end{aligned} \tag{3.57}$$

Note that, while for $T > T_c$ the zero-field behavior of the longitudinal and transverse correlations is identical, for $T < T_c$ the behavior is very different, while for $T=T_c$ the behavior is qualitatively similar but quantitatively different.

Solution on a ring

On a closed ring of N sites the n-vector model is represented by the Hamiltonian,

$$\mathscr{H}=-H\sum_{i=1}^{N}S_i^1-J\sum_{i=1}^{N}\vec{S}_i\cdot\vec{S}_{i+1}\,, \tag{3.58}$$

with the periodic boundary condition $\vec{S}_{N+1}=\vec{S}_1$.

The partition function

$$Z_N^{(r)}=\langle\exp(-\beta\mathscr{H})\rangle$$

can be calculated by the same method as for the chain. The difference is that $\vec{S}_1$ is coupled both to $\vec{S}_2$ and to $\vec{S}_N$ and the integration over $\vec{S}_1$ introduces new terms such as S_N^1 and $\vec{S}_2\cdot\vec{S}_N$. The integration over $\vec{S}_2$ will introduce terms of the type $\vec{S}_3\cdot\vec{S}_N$ so that after integrating over $\vec{S}_1$, then $\vec{S}_2,\ldots,\vec{S}_p$, the partition function takes the form

$$Z_N^{(r)}=\left\langle [A_p+B_pS_{p+1}^1+(C_p+D_pS_{p+1}^1)S_N^1+E_p\vec{S}_N\cdot\vec{S}_{p+1}]\exp\left[h\sum_{p+1}^{N}S_i^1+\tilde{J}\sum_{p+1}^{N-1}\vec{S}_i\cdot\vec{S}_{i+1}\right]\right\rangle_{(\vec{S}_{p+1},\ldots,\vec{S}_N)}\,. \tag{3.59}$$

The coefficients $A_{p+1},B_{p+1},C_{p+1},D_{p+1},E_{p+1}$ are linear functions of A_p,B_p,C_p,D_p,E_p:

$$\begin{bmatrix}A_{p+1}\\B_{p+1}\\C_{p+1}\\D_{p+1}\\E_{p+1}\end{bmatrix}=\underline{M}\begin{bmatrix}A_p\\B_p\\C_p\\D_p\\E_p\end{bmatrix}, \tag{3.60}$$

with

$$\underline{M}=\begin{bmatrix}1+\frac{1}{2}h^2 & h & 0 & 0 & 0\\ h\tilde{J} & \tilde{J} & 0 & 0 & 0\\ 0 & 0 & 1+\frac{1}{2}h^2 & h & h\\ 0 & 0 & h\tilde{J} & \tilde{J} & 0\\ 0 & 0 & 0 & 0 & \tilde{J}\end{bmatrix}. \tag{3.61}$$

The initial conditions are

$$A_0=1,\ \ B_0=C_0=D_0=0$$

and $E_0=\tilde{J}$. The last integration step is as follows:

$$Z_N^{(r)}=\langle A_{N-1}+B_{N-1}S_N^1+(C_{N-1}+D_{N-1}S_N^1)S_N^1+E_{N-1}\,|\,S_N\,|^2\exp(hS_N^1)\rangle_{(\vec{S}_N)}\,. \tag{3.62}$$

This yields

$$Z_N^{(r)}=A_{N-1}(1+\tfrac{1}{2}h^2)+B_{N-1}h+C_{N-1}h+D_{N-1}\,, \tag{3.63}$$

so that $Z_N^{(r)}$ can be written in the form

$$Z_N^{(r)}=((1+\tfrac{1}{2}h^2)\ \ h\ \ h\ \ 1\ \ 0)\underline{M}^{N-1}\begin{bmatrix}1\\0\\0\\0\\\tilde{J}\end{bmatrix}, \tag{3.64}$$

where $\underline{M}$ is given by (3.61).

This expression can be simplified by the standard procedure of expressing $Z_N^{(r)}$ in terms of the eigenvalues and eigenvectors of the matrix $\underline{M}$. The secular equation factorizes to give a linear equation and two quadratics that are the same as for the chain [Eq. (3.11)]. The eigenvalues are equal to λ_0 and λ_1 in Eq. (3.12), each with degeneracy 2, and to $\tilde{J}$. A straightforward but somewhat tedious calculation with the matrices of right and left eigenvectors verifies that the partition function can be written exactly as

$$Z_N^{(r)}=\lambda_0^N+\lambda_1^N-\tilde{J}^N\ . \tag{3.65}$$

Thus, with $a=2$, $K_1=\frac{1}{2}h^2$, and $K_p=\tilde{J}$, we recover the result obtained previously for the partition function of equilibrium polymerization on a ring [Eq. (2.19)], where closed polymers were excluded by fiat. Here the exclusion of the closed ring of N bonds, corresponding to the term $\tilde{J}^N$, is accomplished automatically by the limit $n\to 0$.

IV. $n\to 0$ VECTOR MODEL BY RENORMALIZATION-GROUP ANALYSIS

We have shown in the preceding sections that the one-dimensional $n\to 0$ vector model exhibits a phase transition. It is interesting to analyze the model from a renormalization-group approach. We apply a decimation transformation which has been applied previously to the one-dimensional Ising model.[11] By decimating every other spin along the chain we generate a renormalization-group transformation with a change of scale $l'/l=b=2$. In this method new operators are generated through the renormalization-group transformation, as we shall see later, and we have to study a more general $n\to 0$ vector model with the following reduced Hamiltonian:

$$\begin{aligned}\overline{\mathscr{H}}=-\frac{\mathscr{H}}{kT}=\sum_{i=1}^{N}[hS_i^1+L(S_i^1)^2]+\sum_{i=1}^{N-1}\{&\tilde{J}\vec{S}_i\cdot\vec{S}_{i+1}+\Delta S_i^1S_{i+1}^1+K(S_i^1)^2(S_{i+1}^1)^2\\&+M[S_i^1(S_{i+1}^1)^2+(S_i^1)^2(S_{i+1}^1)\}]+\sum_{i=1}^{N}C\ .\end{aligned} \tag{4.1}$$

Exact solution of generalized model

Before applying the decimation method we shall first calculate the exact partition function of this general n-vector model in the limit $n\to 0$, using the same matrix method as in Sec. III. We integrate, to calculate the partition function, over $\vec{S}_1$ then over $\vec{S}_2$ and so on up to $\vec{S}_N$. By integrating over $\vec{S}_1$ the partition function is expressed as

$$\begin{aligned}Z_N^c=\langle e^{\overline{\mathscr{H}}}\rangle_{(\vec{S}_1,\dots,\vec{S}_N)}=\langle\{&(1+\tfrac{1}{2}h^2+L)+[h(\tilde{J}+\Delta)+M]S_2^1\\&+(K+\tfrac{1}{2}\Delta^2+\tilde{J}\Delta+hM)(S_2^1)^2\}\exp\overline{\mathscr{H}}(\vec{S}_2,\dots,\vec{S}_N)\rangle_{(\vec{S}_2,\dots,\vec{S}_N)}\exp(NC)\end{aligned} \tag{4.2}$$

and after integrating over $\vec{S}_1,\vec{S}_2,\dots,\vec{S}_p$, the partition function can be expressed in the form

$$Z_N^c=\langle[A_p+B_pS_{p+1}^1+C_p(S_{p+1}^1)^2]\exp\overline{\mathscr{H}}(\vec{S}_{p+1},\dots,\vec{S}_N)\rangle_{\vec{S}_{p+1}\cdots\vec{S}_N}\exp(NC)\ , \tag{4.3}$$

where the coefficients A_{p+1},B_{p+1},C_{p+1} are linear functions of A_p,B_p,C_p:

$$\begin{bmatrix}A_{p+1}\\B_{p+1}\\C_{p+1}\end{bmatrix}=\underline{M}\begin{bmatrix}A_p\\B_p\\C_p\end{bmatrix} \tag{4.4}$$

with

$$\underline{M}=\begin{bmatrix}1+L+\frac{1}{2}h^2 & h & 1\\ h(\tilde{J}+\Delta)+M & \tilde{J}+\Delta & 0\\ K+\frac{1}{2}\Delta^2+J\Delta+Mh & M & 0\end{bmatrix}. \tag{4.5}$$

The initial conditions are $A_0=1,B_0=C_0=0$ and from Eq. (4.3) we obtain

$$e^{-NC}Z_N^c=A_{p=N}=(1\ \ 0\ \ 0)\underline{M}^N\begin{bmatrix}1\\0\\0\end{bmatrix}\ , \tag{4.6}$$

where $\underline{M}$ is given by (4.5). This expression can be simplified by expressing Z_N^c in terms of the eigenvalues and eigenvectors of the matrix $\underline{M}$. The secular equation is

$$\lambda^3-\lambda^2(\tilde{J}+\Delta+1+\tfrac{1}{2}h^2+L)-\lambda\left[K+2hM+\tfrac{1}{2}\Delta^2+J\Delta+(J+\Delta)\left[\frac{h^2}{2}-1-L\right]\right]$$
$$+(J+\Delta)(K+J\Delta+\tfrac{1}{2}\Delta^2)-M^2=0 \quad (4.7)$$

giving eigenvalues $\lambda_0,\lambda_1,\lambda_2$, where λ_0 is the maximum eigenvalue. In the limit $N\rightarrow\infty$ we obtain the free energy per site

$$f\equiv\lim_{N\rightarrow\infty}(N^{-1}\ln Z_N)=\ln\lambda_0 \ . \quad (4.8)$$

Renormalization-group transformation

In the decimation transformation a central spin $\vec{S}$ coupled to the two neighboring spins $\vec{S}_1$ and $\vec{S}_2$ is replaced by a single bond joining the two "external" spins. The transformation is effected by taking the trace over the internal degrees of freedom of the system, and one is left with a conditional partition function $\psi(\vec{S}_1,\vec{S}_2)$ which can be expressed as

$$\psi(\vec{S}_1,\vec{S}_2)=\langle\exp\{hS^1+L(S^1)^2+\tilde{J}\,\vec{S}\cdot(\vec{S}_1+\vec{S}_2)+\Delta S^1(S_1^1+S_2^1)+K(S^1)^2[(S_1^1)^2+(S_2^1)^2]$$
$$+MS^1[(S_1^1)^2+(S_2^1)^2]+M(S^1)^2(S_1^1+S_2^1)\}\rangle_{(\vec{S})} \ . \quad (4.9)$$

By expanding the exponential and taking the average over $\vec{S}$ in the limit $n\rightarrow 0$, retaining only nonzero averages $\langle(S^\alpha)^2\rangle=1$, we obtain

$$\psi(\vec{S}_1,\vec{S}_2)=1+L+\tfrac{1}{2}h^2+(\tilde{J})^2\vec{S}_1\cdot\vec{S}^2+(\Delta^2+2\Delta\tilde{J})S_1^1S_2^1+[h(\Delta+\tilde{J})+M](S_1^1+S_2^1)$$
$$+(\tfrac{1}{2}\Delta^2+\tilde{J}\Delta+K+hM)[(S_1^1)^2+(S_2^1)^2]+M^2(S_1^1S_2^1)^2$$
$$+M(\Delta+J)[(S_1^1)^2S_2^1+S_1^1(S_2^1)^2] \ . \quad (4.10)$$

We must now express $\psi(\vec{S}_1,\vec{S}_2)$ in the exponential form $\exp[\rho(\vec{S}_1,\vec{S}_2)]$ in such a way that, for any function $f(\vec{S}_1,\vec{S}_2)$, the equality

$$\langle f(\vec{S}_1,\vec{S}_2)\psi(\vec{S}_1,\vec{S}_2)\rangle_{\vec{S}_1\vec{S}_2}=\langle f(\vec{S}_1,\vec{S}_2)\exp[\rho(\vec{S}_1,\vec{S}_2)]\rangle_{\vec{S}_1\vec{S}_2} \quad (4.11)$$

is satisfied. We also want $\rho(\vec{S}_1,\vec{S}_2)$ to be of the same form as the original Hamiltonian:

$$\rho(\vec{S}_1,\vec{S}_2)=h''(S_1^1+S_2^1)+L''[(S_1^1)^2+(S_2^1)^2]+\tilde{J}'\vec{S}_1\cdot\vec{S}_2+\Delta'S_1^1S_2^1+K'(S_1^1)^2(S_2^1)^2$$
$$+M'[S_1^1(S_2^1)^2+(S_1^1)^2S_2^1]+C' \ . \quad (4.12)$$

We expand $\exp[\rho(\vec{S}_1,\vec{S}_2)]$ and retain only the terms which, when multiplied by any function of $\vec{S}_1,\vec{S}_2$ and averaged over $\vec{S}_1,\vec{S}_2$ in the limit $n\rightarrow 0$, give nonzero contributions. For instance, a term $(S_1^1)^3$ can never give a nonzero contribution when multiplied by any term of the form $(S_1^\alpha)^p(S_2^\beta)^q$ (for $p,q\geq 0$) and is thus not retained. We get the following expression:

$$\exp[\rho(S_1,S_2)]=\Bigg\{1+h''(S_1^1+S_2^1)+(L''+\tfrac{1}{2}h''^2)[(S_1^1)^2(S_2^1)^2]+\tilde{J}'(\vec{S}_1\cdot\vec{S}_2)+(\Delta'+h'')S_1^1S_2^1$$
$$+K'+\tfrac{1}{2}(\Delta)^2+\tilde{J}'\Delta'+L''^2+2M'h'+h''^2\left[\frac{h''^2}{4}+\Delta'+\tilde{J}'+L''\right](S_1^1S_2^1)^2$$
$$+\left[M'+h'\left[L''+\tilde{J}'+\Delta'+\frac{h''^2}{4}\right]\right][(S_1^1)^2S_2^1+S_1^1(S_2^1)^2]\Bigg\}\exp C' \ . \quad (4.13)$$

Imposing the condition (4.11) determines the coupling constants in (4.13), as given in (4.15), below. The following renormalization-group equation for Z_N then follows:

$$Z_N=\langle\exp\overline{\mathcal{H}}\rangle=\langle\exp\overline{\mathcal{H}}'\rangle$$

with

$$\overline{\mathcal{H}}'=\sum_{j=1}^{N/2-1}\rho(\vec{S}_j,\vec{S}_{j+1})+\sum_{j=1}^{N/2}[hS_j^1+L(S_j^1)^2] \quad (4.14)$$

so that $\overline{\mathcal{H}}'$ has the same form as $\overline{\mathcal{H}}$ with new parameters $(h',L',\ldots)$.

From the equations (4.10)–(4.13) the recursion relations between the parameters h', L', $\tilde{J}'$, Δ', K', M', C' and h, L, $\tilde{J}$, Δ, K, M, C are deduced and written in terms of

$$\begin{aligned} &A \equiv 1+\tfrac{1}{2}h^2+L \ , \\ &x \equiv \tilde{J}+\Delta \ , \qquad (4.15) \\ &y \equiv K+\tilde{J}\Delta+\tfrac{1}{2}\Delta^2 \ . \end{aligned}$$

The set of recursion relations is given by

$$h'=h+2h'' \ ,$$

where

$$h''=(hx+M)/A \ ,$$

$$L'=L+2L'' \ ,$$

where

$$\begin{aligned} &L''=(y+hM)/A \ , \\ &\tilde{J}'=\tilde{J}^2/A \ , \\ &x'=x^2/A-h''^2 \ , \qquad (4.16) \\ &M'=Mx/A-h''\left[L''+\frac{h''^2}{4}+x\right] \ , \\ &y'=M^2/A-L''^2-2M'h''^2\left[\frac{h''^2}{4}+x+L''\right] \ , \end{aligned}$$

and

$$C'=2C+\ln A \ .$$

We see that the recursion relation for $\tilde{J}$ is disconnected from the others, which reflects the fact that the free energy depends only on x, y, h, L, M as can be seen from the exact solution [Eq. (4.7)]. In the thermodynamic limit $N\rightarrow\infty$, the renormalization-group equation [Eq. (4.14)] can be rewritten in terms of the free energy per site $f(h,L,x,y,M,C)$,

$$f(h,L,x,y,M,C)=\tfrac{1}{2}f(h',L',x',y',M',C') \ , \qquad (4.17)$$

where the primed variables are given in terms of the unprimed by (4.16).

Analysis of the recursion relations

We first consider the simple case where initially $h=0$, $x=\tilde{J}\neq 0$, and $y=L=M=C=0$. When we iterate the renormalization transformation, all parameters stay zero except $\tilde{J}$, which obeys the simple recursion relation

$$\tilde{J}'=\tilde{J}^2 \ , \qquad (4.18)$$

so that if $\tilde{J}=1$ it stays equal to one. This fixed point is unstable so that when $\tilde{J}<1$ the successive values of $\tilde{J}$ go towards $\tilde{J}=0$, which is a stable fixed point, and when $\tilde{J}>1$ the successive values of $\tilde{J}$ go towards $\tilde{J}=\infty$ which is another stable fixed point. Thus, $\tilde{J}=1$ corresponds to a crictical point. The linearized recursion relation $(\tilde{J}'-1)=2(\tilde{J}-1)$ leads to a critical exponent

$$\nu^{-1}=(\ln 2/\ln b)=1$$

which says that in one dimension the radius of a polymer of N monomers with excluded volume behaves like $R\sim N^{\nu=1}$. Renormalization-group transformations allow one, in principle, to calculate the free energy $f(\tilde{J})$. When $\tilde{J}$ is less than 1 the successive iterations relate $f(\tilde{J})$ to $f(0)$ as shown by Eq. (4.18) and $f(\tilde{J})$ is then equal to $2^{-p}f(0)=0$. At $\tilde{J}=1$, $f(\tilde{J})=2^{-p}f(1)$ and thus $f(1)=0$. For $\tilde{J}>1$ we have $f(\tilde{J})=2^{-p}f(\tilde{J}^{2^p})$ from which we can conclude that $f(\tilde{J})=A\ln\tilde{J}$. To determine $f(\tilde{J})$ completely it is necessary to calculate $f(\tilde{J},h)$ and then take the limit $h\rightarrow 0$.

We now consider the more general case where the parameters are nonzero. Even when we start with only h and $\tilde{J}$ nonzero (which, incidentally, corresponds to the physical situation of equilibrium polymerization), all the parameters take nonzero values after a few iterations. In the full five-parameter space there are three fixed manifolds P_1^*, P_2^*, and P_3^*:

P_1^* $(x=0,\ y=0,\ M=0;\ h,\ L$ arbitrary$)$

P_2^* $(h=0,\ y=0,\ M=0,\ x=\infty;\ L$ arbitrary$)$

P_3^* $(x=A,\ y=Ah^2,\ M=-Ah;\ L,\ h$ arbitrary$)$.

P_1^* is a "high-temperature" fixed surface, P_2^* is a low-temperature fixed line, and P_3^* is a (doubly) unstable fixed surface responsible for the critical behavior of the model.

In the vicinity of any point on the fixed point manifold P_1^*, characterized by a choice of h and L, if we expand the recursion relations in the small excursions from the chosen fixed point, δh, δL, δx, δy, δM, then the linearized recursion relations may be expressed in the matrix form

$$\begin{bmatrix} \delta h' \\ \delta L' \\ \delta x' \\ \delta y' \\ \delta M' \end{bmatrix} = \begin{bmatrix} 1 & 0 & \dfrac{2h}{A} & 0 & \dfrac{2}{A} \\ 0 & 1 & 0 & \dfrac{2}{A} & \dfrac{2h}{A} \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} \delta h \\ \delta L \\ \delta x \\ \delta y \\ \delta M \end{bmatrix} , \qquad (4.19)$$

where $A=1+L+\frac{1}{2}h^2$. The eigenvalues are easily seen by inspection to be 1, 1, 0, 0, 0.

No meaningful linearization is possible in the vicinity of the low-temperature fixed point manifold

P_2^* (at least not in terms of the variables h,L,x,y,M). Near P_2^* the recursion relations can be conveniently expressed to lowest order in the form

$$\begin{aligned} h' &= \frac{2(hx+M)}{1+L} , \\ \delta L' &= \delta L + \frac{2\delta y}{1+L} , \\ x' &= x^2 , \\ y' &= -2\left[\frac{hx}{1+L}\right]\left[\frac{Mx+hx^2}{1+L}\right]^2 , \\ M' &= \frac{-hx}{1+L} , \end{aligned} \tag{4.20}$$

where we have neglected terms higher than first order in h, δL, y, M that do not contain factors of x.

In the vicinity of P_3^* the recursion relations become

$$\begin{bmatrix} \delta h' \\ \delta L' \\ \delta x' \\ \delta y' \\ \delta M' \end{bmatrix} = \begin{Bmatrix} 3 & 0 & \frac{2h}{A} & 0 & \frac{2}{A} \\ -2h & 1 & 0 & \frac{2}{A} & \frac{2h}{A} \\ -h & -1 & 2 & 0 & 0 \\ -h^3 & -h^2 & 0 & 0 & -2h \\ h^2-A & h & 2h & 0 & 0 \end{Bmatrix} \begin{bmatrix} \delta h \\ \delta L \\ \delta x \\ \delta y \\ \delta M \end{bmatrix} , \tag{4.21}$$

where $A=1+L+\frac{1}{2}h^2$. The eigenvalues are found to be 2,2,1,1,0, independent of h and L. We shall concentrate here on the fixed point of interest for the simple Hamiltonian introduced in Sec. III and for equilibrium polymerization: $h=L=M=y=0$, $\tilde{J}=x=1$. A more complete study in the full parameter space will be presented in a future publication. Close to this fixed point the linearized recursion relations can be expressed in the form

$$\begin{aligned} (x'-1-L'-y') &= 2(x-1-L-y) , \\ h'+M' &= 2(h+M) , \\ h'+2M' &= 1(h+2M) , \\ L'+2y' &= 1(L+2y) , \\ y' &= 0y . \end{aligned} \tag{4.22}$$

Thus, if we make a small change that keeps $M=L=y=0$, but makes h and/or $\tilde{J}-1=x-1$ nonzero, then L and y remain zero, as does Δ, so that $\tilde{J}=x$ remains true, but $x'-1$, M', and h' are all nonzero. It is convenient to express the dependence of the singular part of the free energy in terms of the scaling variables in (4.22):

$$f_s(x-1-L-y,M+h,2M+h) .$$

After iterating the transformation a large number of times (say p) the following equation results:

$$f_s(\tilde{J}-1,h,h)=\frac{1}{2^p}f_s[2^p(\tilde{J}-1),2^p h,h] . \tag{4.23}$$

By choosing p large enough and $(\tilde{J}-1)$ and h small enough, we get the following scaling form for $f_s(\tilde{J},h,h)\equiv\tilde{f}_s(\tilde{J},h)$:

$$\tilde{f}_s(\tilde{J},h)=(\tilde{J}-1)g_{\pm}\left[\frac{h}{|\tilde{J}-1|}\right] , \tag{4.24}$$

where

$$g_{\pm}=f_s\left[1,\frac{h}{(J-1)},0\right] . \tag{4.25}$$

Equation (4.24) is of exactly the same form as (3.16), obtained from the exact solution, and gives $\alpha=1,\Delta=1$. The decimation renormalization-group transformation in which the "spins" are not renormalized leads to the consequence that the correlation function $\langle S_i^1 S_j^1\rangle$ at the critical point $\tilde{J}=1$ does not depend on distance $i-j$ which corresponds to a critical exponent $\eta=1$ as shown in Sec. III from the analysis of the exact solution of the one-dimensional $n\to 0$ vector model.

The renormalization-group transformation can also be used to calculate the free energy from any value of h,L,x,y,M. Starting with the initial values $h^{(0)}=h$, $L^{(0)}=L$, $x^{(0)}=x$, $y^{(0)}=y$, $M^{(0)}=M$, the renormalization trajectory approaches, after several iterations, the stable high-temperature fixed surface P_1^* with $x=\epsilon_1$, $y=\epsilon_2$, $M=\epsilon_3$, where ϵ_i is very small so that

$$f(h,L,x,y,M,C=0) =\frac{1}{2^p}f(h^{(p)},L^{(p)},\epsilon_1,\epsilon_2,\epsilon_3,C^{(p)}) . \tag{4.26}$$

We know that

$$f(h^{(p)},L^{(p)},\epsilon_1,\epsilon_2,\epsilon_3,C^{(p)})\sim\ln A^{(p)}+O(\vec{\epsilon}) \tag{4.27}$$

with

$$C^{(p)}=2^{p-1}\ln A^{(0)}+2^{p-2}\ln A^{(1)}+\cdots+\ln A^{(p-1)} \tag{4.28}$$

and from Eq. (4.26) we obtain

$$f(h,L,x,y,M,C=0)\simeq\sum_{n=0}^{p-1}\frac{\ln A^{(n)}}{2^{n+1}}+\frac{\ln A^{(p)}}{2^p} . \tag{4.29}$$

This formula is approximate because of the corrections of order $\vec{\epsilon}$ in (4.27), but gives reasonable results. To calculate f exactly we have to iterate up to $p=\infty$, where $c_i=0$, so that f is expressed as an infinite sum

$$f(h,L,x,y,M,C=0)=\sum_{n=0}^{\infty}\frac{\ln A^{(n)}}{2^{n+1}} \qquad (4.30)$$

with

$$A^{(n)}=1+\tfrac{1}{2}(h^{(n)})^2+L^{(n)} \,. \qquad (4.31)$$

The expression (4.29) has been applied with $p=20$ and for $\tilde{J}^{(0)}=J=0.18$, $h^{(0)}=h=0.1$ with the result

$$f(\tilde{J}=0.8,h=0.1)=0.037\,813\,5 \,.$$

The exact value given by Eq. (4.8) is 0.037 814. We also obtained another check, namely,

$$f(h=0.1,L=0.1,x=0.85,y=0.141\,25\,,M=0.1)$$
$$=0.258\,794\,3$$

when the exact value given by Eq. (4.8) is 0.258 795.

V. CONNECTION WITH THE ZIMM-BRAGG MODEL AND WITH THE ISING MODEL

We introduce a second model of polymerization in one dimension (model II) which corresponds exactly to the Zimm-Bragg model[13] of the helix-coil transition for their parameter μ equal to one. In this model (model II) the N sites of a chain can be in two possible states, active or inactive (helix or coil), and adjacent active sites are *necessarily* bonded and form "polymers" [in the Zimm-Bragg model a one-dimensional polypeptide is made of helix portions (polymers) separated by coiled portions (nonpolymerized monomers)]. To a polymer of n sites we associate a weight $\tilde{K}_1\tilde{K}_p^{n-1}$ (for correspondence with Zimm-Bragg model $\tilde{K}_1=\sigma s,\tilde{K}_p=s$). The partition function $\tilde{Z}_N^c$ is written

$$\tilde{Z}_N^c(\tilde{K}_1,\tilde{K}_p)=\sum_{N_b,N_p}\tilde{K}_1^{N_p}\tilde{K}_p^{N_b}\tilde{\Gamma}_N^{(c)}(N_b,N_p)\,, \qquad (5.1)$$

where $\tilde{\Gamma}_N^{(c)}(N_b,N_p)$ is the number of ways to put N_p polymers with N_b closed bonds on a chain of N sites and where two one-site polymers cannot be adjacent. The partition function can be calculated exactly by the matrix method, as done by Zimm and Bragg, with the result

$$\tilde{Z}_N^c=\frac{\lambda_0^N(\lambda_1-1-\tilde{K}_1)+\lambda_1^N(-\lambda_0+1+\tilde{K}_1)}{\lambda_1-\lambda_0}\,, \qquad (5.2)$$

where λ_0 and λ_1 are the larger and smaller roots of the equation

$$\lambda^2-\lambda(1+\tilde{K}_p)+(\tilde{K}_p-\tilde{K}_1)=0 \,. \qquad (5.3)$$

In the large N limit the thermodynamic potential

$$\tilde{f}=\frac{\ln\tilde{Z}_N^c}{N}$$

is deduced from Eqs. (5.2) and (5.3), and is equal to

$$\tilde{f}=\ln\lambda_0$$
$$=\ln\left\{\frac{(1+\tilde{K}_p)}{2}+\left[\left[\frac{(1-\tilde{K}_p)}{2}\right]^2+\tilde{K}_1\right]^{1/2}\right\} . \qquad (5.4)$$

The two polymerization models (model I introduced in Sec. II and model II) lead to similar expressions for the partition functions Z_N^c and $\tilde{Z}_N^c$ [see Eqs. (2.6)—(2.8) and (5.2) and (5.3)]. The expressions for the two partition functions Z_N^c and $\tilde{Z}_N^c$ become identical if the following relations between K_1,K_p, $\underline{a}$ and $\tilde{K}_1,\tilde{K}_p$ are satsified:

$$\tilde{K}_1=K_1-K_1K_p(1-a)\,,$$
$$\tilde{K}_p=K_1+K_p \,. \qquad (5.5)$$

The polymerization model II corresponds exactly to the one-dimensional Ising model of magnetism.[11] On a chain of N sites a spin $S_i^z=\pm 1$ is associated to each site and the energy associated to a configuration of ± 1 spins is given by the Hamiltonian

$$\mathcal{H}=-J\sum_{i=1}^{N-1}S_i^zS_{i+1}^z-H\sum_{i=1}^{N}S_i^z \,. \qquad (5.6)$$

There is an exact mapping of the states of the Ising model with the states of the polymerization model if we suppose that the sites with spin + 1 are active and the sites with spin − 1 are inactive. To a state with a given assignment of up and down spins is associated a set of polymers of one or more sites, consisting of the blocks of up spins, dissolved in a solvent of inactive monomers, corresponding to the down spins. The weight associated to a polymer of $\underline{n}$ sites is equal to $\exp(-4\beta J+2n\beta H)$ and the partition function Z_N(Ising) is written

$$Z_N^c(\text{Ising})=\exp[(N-1)\beta J-N\beta H]\sum_{N_p,N_b}[\exp(-4\beta J+2\beta H)]^{N_p}[\exp(+2\beta H)]^{N_b}\tilde{\Gamma}_N^c(N_b,N_p)\,, \qquad (5.7)$$

where we have neglected the edge effects which are absent for a ring, and where $\tilde{\Gamma}_N^c(N_b,N_p)$ has been defined previously.

We see that

$$Z_N^{c(\text{Ising})}(\beta J,\beta H)=\exp N(\beta J-\beta H)\tilde{Z}_N^{c}(\tilde{K}_1,\tilde{K}_p) \tag{5.8}$$

for N large with

$$\tilde{K}_1=\exp(-4\beta J+2\beta H)\;,$$
$$\tilde{K}_p=\exp(+2\beta H)\;, \tag{5.9}$$

and we recover, using Eq. (5.4), for N large the Ising model free energy per spin

$$\frac{F}{N}=f=-J-kT\ln\left[\cosh\left[\frac{H}{kT}\right]+\left[\sinh^2\frac{H}{kT}+e^{-4J/kT}\right]^{1/2}\right]\;. \tag{5.10}$$

From the connection with the Ising model we understand better how the first-order polymerization transition when K_p goes through one for $K_1=0$ is analogous to the first-order transition in a one-dimensional magnet at $T=0$ or $J=\infty$ when the magnetic field goes from 0^+ to 0^-.

VI. DISCUSSION

In the limit of zero initiation constant $K_1\rightarrow 0$, equilibrium polymerization exhibits a phase transition in any dimension. This transition is "critical" in the sense that at the transition very long polymers appear with critical scaling properties[17] with a mean radius which varies as a function of P like $R\sim P^{\nu}$. The exponent ν depends on dimension ($\nu\simeq 0.6$ in $d=3$, while $\nu\simeq 0.75$ in $d=2$, and $\nu=1$ in $d=1$).[9] The departure from the random walk behavior $R\sim P^{1/2}$ is greater at lower dimension. The critical effect becomes so important at $d=1$ that the polymerization transition, which is "second order" for $d=2$ and $d=3$ in the sense that the fraction Φ of monomers incorporated into polymers is continuous, becomes "*first order*" with a jump in ϕ at $K_p=K_p^c=1$.

Although the transition studied here occurs at nonzero temperature ($K_p=1$), it is not a violation of Landau's argument[10] for the nonexistence of phase transitions in one dimension because the limit $K_1\rightarrow 0$ corresponds, for nonzero T, to an infinite energy for activation of the monomer. It is well known that phase transitions can occur in one-dimensional systems in which infinite energies are allowed for some states.

The reason for the qualitative difference between $d=1$ and $d>1$ can be understood in terms of simple Flory-Huggins[18]-type arguments. It is well established that the number of polymers with n bonds and one end fixed at the origin of an infinite lattice has the asymptotic form

$$N_n\sim\mu^n \tag{6.1}$$

for n large, where μ is a number characteristic of the lattice, surely lying in the range $\frac{1}{2}q$ to $q-1$, where q is the coordination number of the lattice. Thus, the statistical weight of all polymers with n bonds and one end fixed at the origin at

$$W_n^0\simeq(K_p\mu)^n\;, \tag{6.2}$$

from which it clearly follows that

$$K_p^c\mu=1\;. \tag{6.3}$$

When $K_p\mu>1$ chain propagation proceeds until a nonzero fraction of all the sites on the lattice are polymerized. If μ^{eff} is the effective value of μ at a given value of Φ, then polymerization stops when $[K_p\mu^{\text{eff}}(\Phi)]=1$. The Tobolsky-Eisenberg theory corresponds (for $K_1=0$) to the Flory estimate $\mu^{\text{eff}}=(1-\Phi)\mu$. The crucial difference of the one-dimensional problem is now easy to see. For $d=1$, $\mu=1$, and $K_p^c=1$ is larger than for $d=2$, 3, etc. However, if a polymer propagates to fill a nonzero fraction of the lattice, this does *not* reduce its effective μ below unity in one dimension, since there is no way for the polymer to fold back and encounter itself. As a result, propagation proceeds until the entire lattice is occupied by polymer.

Some early works can be mentioned in relation to the present one. The analogy between equilibrium polymerization and the helix-coil transition has been mentioned by Oosawa[3] in the context of equilibrium polymerization of proteins into filamentous structures. Tobolsky[1,19] has introduced a one-dimensional model for liquid sulfur polymerization identical to our model I. Balian and Toulouse[15] studied the n-vector model in one dimension with similar results to ours $n\rightarrow 0$. The importance of the effect of dimensionality on equilibrium polymerization makes clearer the fact that equilibrium polymerization can be viewed as a critical phenomenon. Earlier, before the widespread acceptance of this point of view, Tobolsky,[19] after introducing and solving the one-dimensional model of sulfur polymerization, tried to match the final expressions with the expressions he had obtained previously through the approximate Tobolsky-Eisenberg theory. We have shown that these two theories cannot be matched, as they describe polymerization in $d=1$ and in $d>4$ dimensions and the transition is first order in $d=1$ and second order in $d>1$. (We have shown that Tobolsky-Eisenberg is a mean-field theory which becomes adequate for sufficiently high dimension $d>4$.) The n-vector model was originally studied as a function of n by Stanley.[20] The connections of the $n\rightarrow 0$ limit with the statistics of polymers and polymer solutions were first pointed out by de Gennes[21] and Des Cloizeaux,[22] respectively. Additional references to the $n\rightarrow 0$ vector model and polymer statistics can be found in Refs. 6 and 16. Recently, Gujrati[23] has also considered the $n\rightarrow 0$ vector model and polymerization with conclusions similar to our own. The work of Rys and Helfrich[24] should also be noted.

Although the study of equilibrium polymerization in one dimension may seem somewhat academic, it is not out of the question that such a process might actually be realized experimentally. Polymerization reactions have been carried out in urea and thiourea clathrates[25] which contain long, one-dimensional channels that are sufficiently isolated from one another to prevent cross linking. These reactions were carried out far from equilibrium, and there is some question whether appropriate host lattices can be found for polymers which are in chemical equilibrium with their monomers. The recent polymerization of 4-bromostyrene monomers in clathrates of tris-(o-phenylenedioxy)cyclotriphosphazene[26] is an interesting development view of the known equilibrium polymerization of the "living polymer" α-methylstyrene[2] and the potential for adjusting the channel size in the spirocyclotriphosphazenes by varying the spiro side groups.[26] Although somewhat speculative, the possibility is intriguing, and the dramatic difference between the behavior in one and three dimensions would make a bonafide example of equilibrium polymerization in one-dimensional channels of considerable interest.

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