PHYSICAL REVIEW A VOLUME 24, NUMBER 2 AUGUST 1981

# The $n \rightarrow 0$ vector model and equilibrium polymerization

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(Received 17 February 1981)

Equilibrium polymerization of a monomer to long-chain polymers can be usefully described by the $n \rightarrow 0$ limit of the $n$-vector model of magnetism in a small magnetic field. In the molecular-field approximation, the $n \rightarrow 0$ vector model becomes *identical* to the earlier Tobolsky-Eisenberg theory of equilibrium polymerization. An error in an earlier analysis of the $n \rightarrow 0$ vector model is corrected and the consequences for polymerization and polymer solutions are discussed. A curiosity of the $n \rightarrow 0$ vector model—that its free energy does not everywhere satisfy the usual convexity requirements of thermodynamic stability—is also discussed. In an appendix the $n \rightarrow 0$ limit of the cubic discrete $n$-vector model (Hillhorst model) is also shown to be equivalent in mean field to the Tobolsky-Eisenberg theory of equilibrium polymerization.

## I. INTRODUCTION

The formal $n \rightarrow 0$ limit of the $n$-vector model of magnetism has been used as a model for the behavior of single polymers[1] and of polymer solutions.[2] The polymerization of monomers into long-chain polymers under conditions of chemical equilibrium[3,4] constitutes a polymer solution in which interesting transition phenomena can occur.[4,5] The equilibrium polymerization of sulfur[6] and of $\epsilon$-caprolactam and vinyl monomers[4] are examples of inorganic and organic compounds that undergo such polymerization. The equilibrium polymerization of proteins[7] such as actin[8] and tubulin[9] into large supramolecular structures of biological interest also shows transition phenomena reminiscent of second-order phase transitions.

Recently, we have argued[10] that the $n \rightarrow 0$ vector model in a small magnetic field provides a useful description of equilibrium polymerization and that evidence of the nonclassical critical behavior to be expected for the $n \rightarrow 0$ vector model can be seen in the equilibrium polymerization of liquid sulfur. We based our treatment upon the analysis of the $n \rightarrow 0$ vector model by Sarma,[11] and showed that the earlier, very successful treatment of Tobolsky and Eisenberg[6] (TE) was a mean-field approximation in the vicinity of the critical point. Following the acceptance of that letter we discovered an error in Sarma's analysis that necessitates a slight reformulation of our model of equilibrium polymerization, as well as that of the conventional treatment of polymer solutions. As a result of this reformulation, the $n \rightarrow 0$ vector model provides an even more elegant description of equilibrium polymerization.

In this paper we present a corrected analysis of the $n \rightarrow 0$ vector model along the lines of Sarma's treatment that leads to an altered expression for the partition function, distinct from that given by Sarma[11] and used in Ref. 10, but consistent with the earlier treatment by Bowers and McKerrell.[12] We also present a minor modification of our model for equilibrium polymerization that is identical to the $n \rightarrow 0$ vector model under the corrected analysis. We show that the molecular-field approximation to the $n$-vector model becomes *identical*, in the $n \rightarrow 0$ limit, to the Tobolsky-Eisenberg[6] theory of equilibrium polymerization. This result holds true not just close to the critical point, but identically in the independent variables under an appropriate and physically sensible identification of the variables. The required modifications of our polymerization model are so slight that they have almost no effect upon the results quoted in Ref. 10. In particular the results in Figs. 1 and 2 of Ref. 10 are unchanged, and the equation of state and the results quoted in Eqs. (7)–(13) of that paper are unchanged except for the replacement everywhere of $K_1$ by $2K_1$.

In Sec. II we define the Hamiltonian, partition function and free energy per spin of the $n$-vector model and state our corrected formula for the partition function of the $n \rightarrow 0$ limit. We then define our slightly modified model of equilibrium polymerization, obtain the partition function appropriate to it, and give the identification of variables under which it is identical to the $n \rightarrow 0$ vector model. We also briefly review the essentials of the Tobolsky-Eisenberg theory of equilibrium polymerization. In Sec. III we obtain the molecular-field approximation to the $n$-vector model in the $n \rightarrow 0$ limit and show that it is identical to the TE theory under an appropriate identification of variables. We also discuss there, in the context of the molecular-field approximation a curiosity of the $n \to 0$ limit—that the free energy per spin does not satisfy the usual convexity requirements of thermodynamic stability. This is a quite general feature of the $n \to 0$ vector model, not limited to the molecular-field approximation, a point that is pursued further in Sec. V. In Sec. IV we present the corrected analysis of the partition function and free energy of the $n \to 0$ vector model. Section V contains a discussion of the significance of our results for the application of the $n \to 0$ vector model to equilibrium polymerization and polymer solutions. We also present there a conjecture on the region of convexity of the free energy per spin of the $n \to 0$ vector model if nonclassical critical phenomena and scaling describe the critical point.

Completely analogous behavior is obtained for the cubically discrete $n$-vector model introduced by Hillhorst.[13] In the limit $n \to 0$ it gives a model of equilibrium polymerization identical with that presented here. In mean-field theory it also becomes identical, as $n \to 0$, to the theory of Tobolsky and Eisenberg. These results are outlined in Appendix A.

## II. THE $n \to 0$ VECTOR MODEL AND EQUILIBRIUM POLYMERIZATION

Consider first a system of $N$ classical vector "spins" located on the sites of a regular $d = 3$ dimensional lattice and interacting through the Hamiltonian

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

where the sums $\sum_i$ and $\sum_{\langle i,j \rangle}$ are over all sites and all distinct nearest-neighbor pairs $\langle i, j \rangle$ of sites, and where $\vec{S}$ is a classical $n$-component vector spin of norm $\sqrt{n}$,

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

and $S^{(1)}$ is its component parallel to the field $H$.

We define the partition function and free energy of this model as

$$Z = e^{Nf} = \langle e^{-\tilde{\beta}\mathcal{H}} \rangle_{A^N} \equiv \mathrm{Tr}(e^{-\tilde{\beta}\mathcal{H}}), \tag{2.3}$$

where $\tilde{\beta} = 1/k\tilde{T}$ ($k$ is Boltzmann's constant and $\tilde{T}$ is the temperature of the $n$-vector model) and $\langle\, \rangle_{A^N}$ is the angular average of every spin over all solid angles in $n$ dimensions. For spin $i$ this average is

$$\langle \cdot \rangle_A = \frac{\int d\Omega_i^{(n)}(\cdot)}{\int d\Omega_i^{(n)}(1)} = \frac{\int d\Omega_i^{(n)}(\cdot)}{[2\pi^{n/2}/\Gamma(n/2)]}. \tag{2.4}$$

The use of the average rather than the simple integral over all solid angles as the "trace" operator $\mathrm{Tr}(\cdot)$ in Eq. (2.3) corresponds to the addition of a constant to the Gibbs function per spin $f$. In the limit $n \to 0$ this constant diverges, but it does not depend upon the variables $\tilde{T}$ or $H$, and so has no effect on the magnetization or energy of the system as functions of $T$ and $H$. It is convenient to define the dimensionless magnetization and energy per spin, $m$ and $e$, by

$$m = N^{-1}\mathrm{Tr}\Big(\rho \sum_i S_i^{(1)}\Big) = \left(\frac{\partial f}{\partial h}\right)_{\tilde{J}}, \tag{2.5}$$

$$e = N^{-1}\mathrm{Tr}\Big(\rho \sum_{\langle i,j \rangle} \vec{S}_i \cdot \vec{S}_j\Big) = \left(\frac{\partial f}{\partial \tilde{J}}\right)_h, \tag{2.6}$$

where

$$\rho = \exp(-\tilde{\beta}\mathcal{H})/\mathrm{Tr}[\exp(-\tilde{\beta}\mathcal{H})] \tag{2.7}$$

and

$$h = m_0 H/k\tilde{T}, \quad \tilde{J} = J/k\tilde{T}. \tag{2.8}$$

We show in Sec. IV that the partition function $Z$ in (2.3) is given, in the limit $n \to 0$ by the expression

$$Z = \sum_{N_p} \sum_{N_b} \sum_{N_1} (\tilde{J})^{N_b} (h^2)^{N_p} (\tfrac{1}{2})^{N_1} \Gamma(N_p, N_b, N_1, N), \tag{2.9}$$

where $\Gamma(N_b, N_p, N_1, N)$ is the number of distinguishable ways of placing $N_p$ self-avoiding and mutually avoiding open walks (linear "polymers" with excluded volume) containing a total of $N_b$ steps or bonds on a lattice-$N$ sites when exactly $N_1$ of the walks or polymers are single-site walks with no bonds. Equation (2.9) differs from that of Sarma[11] in that it contains single-site walks and these are weighted by an extra factor of $\frac{1}{2}$ compared with all other walks. We use the term "walk" here as synonymous with "linear polymer", that is, without regard to which end of the walk is the start or finish.

Now consider the following model of equilibrium polymerization. The volume consists of $N$ cells, each of volume $v_0$ about equal to a molecular volume, centered on the sites of the regular lattice considered above. Each cell contains a monomer unit (an $S_8$ ring in the case of sulfur) that may be either inactive (closed $S_8$ ring) or active (open $S_8$ unit), in which case it is to be thought of as part of a polymer chain of some length, possibly of length 1. Suppose that the opening of a sulfur ring (activation of monomer) costs an energy (or enthalpy; these are indistinguishable in our lattice model) $\Delta H_1$, but leads to an increased number of internal configurations resulting in an entropy contribution $\Delta S_1$. Suppose further that the opening of a sulfur ring together with its attachment to the end of an already open sulfur chain in an adjacent cell costs energy $\Delta H_p$ and results in an entropy contribution $\Delta S_p'$ due to an increased number of internal configurations. We anticipate that $\Delta H_1 \gg \Delta H_p > 0$ and $\Delta S_1 > \Delta S_p' > 0$. It should be noted that $\Delta S_p'$ does not contain contributions from the number of ways to arrange chains of open $S_8$ units (monomers) on a lattice. These are accounted for in $\Gamma$ in Eq. (2.12), below. This is a significant difference between the model considered here and in Ref. 10 and that of Tobolsky and Eisenberg.[6]

The statistical weight of any given linear polymer consisting of $m$ monomers (and therefore $m$-1 bonds) with a specific (self-avoiding) embedding in the lattice is taken to be

$$\begin{aligned} &K_1 \text{ if } m=1,\\ &2K_1(K_p')^{m-1} \text{ if } m>1, \end{aligned} \tag{2.10}$$

where

$$\begin{aligned} K_1 &= \exp[(T\Delta S_1 - \Delta H_1)/kT],\\ K_p' &= \exp[(T\Delta S_p' - \Delta H_p)/kT]. \end{aligned} \tag{2.11}$$

The prime on $K_p'$ and $\Delta S_p'$ serves as a reminder that these quantities differ from those in the TE theory in that they do not include contributions from the number of ways to arrange chains of $S_8$ units on a lattice. The statistical weight of any closed-loop polymer containing more than one monomer is taken to be zero. This is in keeping with the Tobolsky-Eisenberg theory and is required for the correspondence with the $n \to 0$ vector model. Inclusion of closed rings in a Tobolsky-Eisenberg-type theory introduces a small concentration of low molecular weight rings, but does not significantly alter the transition.

The factor of 2 in Eq. (2.10) for $m > 1$ is required for the correspondence with the $n \to 0$ vector model. It is equivalent to taking the value of $K_p'$ for the first propagation step to be twice that for all others. This may be rationalized as follows. In the first propagation step the newly opened ring may be connected to either end of the already opened ring in the adjacent cell, whereas in every subsequent propagation step the newly opened ring has only one active end of a monomer unit in the next cell to which it can connect. This argument helps to make the factor of 2 in (2.10) plausible, but its ultimate justification is that it makes possible the exact correspondence with the $n \to 0$ vector model.

The (semi-grand) partition function appropriate to this model of equilibrium polymerization can be written as

$$Y = \sum_{N_p} \sum_{N_b} \sum_{N_1} (2K_1)^{N_p} (K_p')^{N_b} (\tfrac{1}{2})^{N_1} \Gamma(N_p, N_b, N_1, N), \tag{2.12}$$

where $N_p, N_b, N_1$ and $\Gamma(N_p, N_b, N_1, N)$ have the same significance as in Eq. (2.9). We thus see that with the identifications

$$\tilde{J} = K_p' \tag{2.13}$$

and

$$\tfrac{1}{2} h^2 = K_1, \tag{2.14}$$

the expressions for $Z$ and $Y$ are identical.

Apart from a trivial change of concentration units from number densities to mole fractions, the only change in the correspondence between the $n \to 0$ vector model and equilibrium polymerization from that given in Ref. 10 is the factor of 2 in Eq. (2.10) and the corresponding factor of $\frac{1}{2}$ in Eq. (2.14) compared with the corresponding expressions in Ref. 10. Of course, the change in the expression for the partition function of each, embodied in Eqs. (2.9) and (2.12) compared with Eq. (4) of Ref. 10, may have far reaching consequences, but it does not affect the correspondence once the factor of 2 is incorporated.

The average values of $N_b$ and $N_p$ are given by

$$\begin{aligned} \langle N_b \rangle &= \tilde{J} \left( \frac{\partial \ln Z}{\partial \tilde{J}} \right)_h,\\ \langle N_p \rangle &= \tfrac{1}{2} h \left( \frac{\partial \ln Z}{\partial h} \right)_{\tilde{J}}. \end{aligned} \tag{2.15}$$

The corresponding fraction of monomers incorporated in polymers $\phi_\mu$, and the fraction remaining as monomers $\phi_\lambda$, are

$$\phi_\mu = \frac{\langle N_b + N_p \rangle}{N} = \tilde{J} e + \tfrac{1}{2} h m, \tag{2.16}$$

$$\phi_\lambda = 1 - \phi_\mu. \tag{2.17}$$

In the Tobolsky-Eisenberg theory of sulfur, concentrations rather than mole fractions are used, but this presents no difficulties. If $c_{00}$ is the initial concentration of $S_8$ rings (monomer) and $c_0$ is the concentration of $S_8$ rings remaining at equilibrium, $c_p$ is the concentration of polymers, and $c_m$ is the concentration of monomers encorporated in polymers, then

$$\frac{c_0}{c_{00}} = \phi_\lambda, \tag{2.18}$$

$$\frac{c_m}{c_{00}} = \phi_\mu, \tag{2.19}$$

and

$$\frac{c_p}{c_{00}} = \frac{\langle N_p \rangle}{N} = \tfrac{1}{2} h m. \tag{2.20}$$

[The quantities $m$ and $e$ defined in Eqs. (2.5) and (2.6) differ from those in Ref. 10 by a factor $v_0$.] The degree of polymerization $P$ is given by

$$P=\frac{c_m}{c_p}=1+\frac{\tilde{J}e}{\frac{1}{2}hm}\,. \tag{2.21}$$

The results of Tobolsky-Eisenberg theory can be summarized by the equations

$$\phi_\mu=\frac{K_1\phi_\lambda}{(1-K_p\phi_\lambda)^2}\,, \tag{2.22}$$

$$\frac{c_p}{c_{00}}=\frac{K_1\phi_\lambda}{1-K_p\phi_\lambda}\,, \tag{2.23}$$

and

$$P=(1-K_p\phi_\lambda)^{-1}, \tag{2.24}$$

where $K_p$ in Eqs. (2.22)–(2 24) differs from that of Tobolsky and Eisenberg by the constant factor $c_{00}$ that accounts for the change in standard state from concentration units to mole fractions. The conservation equation (2.17) leads to the "equation of state" for the Tobolsky-Eisenberg theory:

$$(\phi_\mu+\phi_\lambda)=1=\phi_\lambda\left(1+\frac{K_1}{(1-K_p\phi_\lambda)^2}\right). \tag{2.25}$$

In Sec. III we show that with an appropriate identification of variables the molecular-field approximation to the $n$-vector model becomes identical, in the $n\to 0$ limit, with the theory of Tobolsky and Eisenberg.

## III. MOLECULAR-FIELD APPROXIMATION TO THE $n\to 0$ VECTOR MODEL

In order to obtain the molecular-field approximation to the $n$-vector model, we follow the treatment of Blume, Emery, and Griffiths[14] (BEG) and use the variational principle

$$-k\tilde{T}Nf\le N\phi=\mathrm{Tr}(\rho\mathcal{H})+k\tilde{T}\,\mathrm{Tr}(\rho\ln\rho)\,, \tag{3.1}$$

where, according to (2.3), the angular average over all spins constitutes the trace operation $\mathrm{Tr}(\cdot)$. Equality obtains in Eq. (3.1) if $\rho$ is given by Eq. (2.7). The molecular-field approximation consists of approximating $\rho$ by

$$\rho=\rho_0\equiv\prod_i\rho_i\,, \tag{3.2}$$

with $\rho_i=\rho_1$, independently of $i$. Substituting (2.1) into (3.1) with (3.2) gives for $\tilde{\phi}\equiv\tilde{\beta}\phi$

$$-f_0\equiv\tilde{\phi}=-\tfrac{1}{2}q\tilde{J}(\mathrm{Tr}\,\rho_1S_1^{(1)})^2-h(\mathrm{Tr}\,\rho_1S_1^{(1)})+\mathrm{Tr}(\rho_1\ln\rho_1)\,, \tag{3.3}$$

where $\tilde{J}$ and $h$ are given by (2.8) and $q$ is the coordination number of the underlying lattice ($q=6$ for the three-dimensional simple cubic lattice). Minimizing $\tilde{\phi}$ with respect to $\rho_1$, subject to the constraint that $\mathrm{Tr}\rho_1=1$, we obtain, following (BEG),

$$\rho_1=\exp(-\tilde{\beta}h_1)/\mathrm{Tr}\exp(-\tilde{\beta}h_1)\,, \tag{3.4}$$

with

$$h_1=-(qJm+m_0H)S_1^{(1)}\,, \tag{3.5}$$

where $m$ is given by (2.5) and can also be written

$$m=\mathrm{Tr}(\rho_1S_1^{(1)})\,. \tag{3.6}$$

In all of Eqs. (3.3)–(3.6) the trace operation is given by the angular average in (2.4).

Our development in Eqs. (3.1)–(3.6) closely parallels that in Sec. III of (BEG). It should be noted that in writing (3.3)–(3.6) we have assumed that $(\mathrm{Tr}\,\rho_1\vec{S}_1)$ is a vector pointing in the direction of the magnetic field so that

$$(\mathrm{Tr}\,\rho_1\vec{S}_1)\cdot(\mathrm{Tr}\,\rho_1\vec{S}_1)=(\mathrm{Tr}\,\rho_1S_1^{(1)})^2 \tag{3.7}$$

and

$$(\mathrm{Tr}\,\rho_1\vec{S}_1)\cdot\vec{S}_1=(\mathrm{Tr}\,\rho_1S_1^{(1)})S_1^{(1)}\,.$$

This is a reasonable assumption given the isotropic interaction term in (2.1).

From (3.3)–(3.5) we obtain, for $\tilde{\phi}$,

$$\tilde{\phi}=\tfrac{1}{2}q\tilde{J}m^2-\ln(\mathrm{Tr}\,e^{-\tilde{\beta}h_1})\,, \tag{3.8}$$

where

$$\mathrm{Tr}\,e^{-\tilde{\beta}h_1}=\langle\exp[(q\tilde{J}m+h)S_1^{(1)}]\rangle_A \tag{3.9}$$

and the angular average $\langle\ \rangle_A$ is given by (2.4).

The average in (3.9) can be evaluated explicitely by expanding the exponential and evaluating the resulting averages of $(S_1^{(1)})^j$. The averages are zero for odd powers of $S_1^{(1)}$ and the averages for even powers are found to be (see Appendix B)

$$\langle(S_1^{(1)})^{2k}\rangle_A=2\left(\frac{\Gamma\left(\frac{n+2}{2}\right)\Gamma\left(\frac{2k+1}{2}\right)}{\Gamma(\frac{1}{2})\,\Gamma\left(\frac{2k+n}{2}\right)}\right)n^{(k-1)}. \tag{3.10}$$

If we now take the formal limit $n\to 0$ in (3.10) for $k=0,1,2,\ldots$, we obtain the well-known[11] result for the $n\to 0$ vector model that

$$\langle(S_1^{(1)})^{2k}\rangle_A=\begin{cases}1 & (k=0,1)\\ 0 & (k>1).\end{cases} \tag{3.11}$$

Inserting this into the expansion of (3.9) we obtain

$$\mathrm{Tr}(e^{-\tilde{\beta}h_1})=1+\tfrac{1}{2}(q\tilde{J}m+h)^2\,, \tag{3.12}$$

and evaluating $\tilde{\phi}$ in (3.8) and $m$ and $e$ in (2.5) and (2.6) we obtain

$$\tilde{\phi}=\tfrac{1}{2}q\tilde{J}m^2-\ln[1+\tfrac{1}{2}(q\tilde{J}m+h)^2]\,, \tag{3.13}$$

$$m=\frac{q\tilde{J}m+h}{1+\frac{1}{2}(q\tilde{J}m+h)^2}\,, \tag{3.14}$$

$$e=\tfrac{1}{2}qm^2\,. \tag{3.15}$$

Alternatively, the molecular-field approximation to the $n$-vector model can be obtained exactly for all values of $n$ in terms of Bessel functions. The $n \to 0$ limit gives the same results. This is shown in Appendix C.

Apparent in Eq. (3.14) is a curious and apparently ubiquitous[15] feature of the $n \to 0$ limit: the free energy $f(\tilde{J}, h)$ does not satisfy the usual convexity requirements of thermodynamic stability. Specifically, $m$ decreases with $h$ as $h \to \infty$, varying as $m \sim 2/h$. We discuss this feature at greater length at the end of this section and in Sec. V. Here we merely remark that this causes no difficulties in working out the properties of the $n \to 0$ vector model as a function of $\tilde{J}$ and $h$ and is not reflected in any nonphysical instability in the corresponding model of equilibrium polymerization.

Equation (3.14) can be solved for $h$ as a function of $m$ and $\tilde{J}$. The solution can be expressed in the form

$$h = \frac{2m}{1 \pm (1 - 2m^2)^{1/2}} - q\tilde{J}m, \tag{3.16}$$

where the + sign is appropriate for small $h$ and $q\tilde{J}$, specifically when

$$|h| \leqslant \sqrt{2}\,(1 - \tfrac{1}{2} q\tilde{J}). \tag{3.17}$$

Alternatively, (3.16) may be written

$$(q\tilde{J}m + h) = \frac{1}{m}[1 \mp (1 - 2m^2)^{1/2}], \tag{3.18}$$

where the upper or lower sign is chosen in accordance with (3.16).

According to (2.16), together with (3.15), $\phi_\mu$ is given by

$$\phi_\mu = \tfrac{1}{2} m (q\tilde{J}m + h). \tag{3.19}$$

With (3.18) and (2.17), this gives

$$\phi_\mu = \tfrac{1}{2}[1 \mp (1 - 2m^2)^{1/2}], \tag{3.20}$$

$$\phi_\lambda = \tfrac{1}{2}[1 \pm (1 - 2m^2)^{1/2}]. \tag{3.21}$$

We now make the identification [cf. Eqs. (2.13) and (2.14)]

$$q\tilde{J}(\equiv qK_p') = K_p, \quad \tfrac{1}{2}h^2 = K_1, \tag{3.22}$$

and show that Eq. (3.16) for the $n \to 0$ vector model is equivalent to Eqs. (2.22) and (2.25) for the Tobolsky-Eisenberg theory. With (3.22), Eq. (3.16) may be written as

$$\sqrt{2K_1} = m\left(\frac{1 - K_p\phi_\lambda}{\phi_\lambda}\right), \tag{3.23}$$

where we have used (3.21). Equations (3.20) and (3.21) imply that $\phi_\lambda + \phi_\mu = 1$ and that

$$\phi_\lambda \phi_\mu = \tfrac{1}{2} m^2. \tag{3.24}$$

Squaring both sides of (3.23) and using (3.24) we recover (2.22), which implies (2.25). Similarly, using (3.22) and (3.23) we easily obtain (2.23) and (2.24).

This completes the demonstration that the molecular-field approximation to the $n$-vector model in the $n \to 0$ limit is identical with the Tobolsky-Eisenberg theory of equilibrium polymerization under the indentification (3.22). The identification of $K_1$ in (3.22) is identical with that in (2.14). The identification of $q\tilde{J} = qK_p'$ with $K_p$ of TE theory is equivalent to the assertion that the number of self-avoiding walks of $b$ bonds starting from the origin is $\sim q^b$. This is, of course, incorrect, the correct number being of the form[12,16] $\sim b^{\gamma-1}\mu^b$, where $\mu < q$, but this estimate is in keeping with the molecular-field approximation which neglects correlations between spins.

We return now to the lack of convexity of $f(\tilde{J}, h)$. The approximate potential $f \equiv -\phi_0$ defined by (3.1) with (3.2) is to be thought of as a function of the independent variables $\tilde{J}$ and $h$, and is given by (3.13) with the understanding that $m$ is to be determined by $\tilde{J}$ and $h$ through (3.14). If more than one solution exists for given $\tilde{J}$, $h$, then the one(s) giving the minimum value of $\phi$ is (are) to be chosen. With this understanding, $\tilde{\phi}$, $m$, and $e$ are well defined continuous functions of $\tilde{J}$ and $h$, except at $h = 0$, $q\tilde{J} > 1$, where $m$ is discontinuous. The failure of the resulting $f_0(\tilde{J}, h)$ to satisfy convexity leads to no difficulty in locating the phase transition nor to any ambiguity about the properties of the model, although some of the properties are rather unusual. For example, the spontaneous magnetization is found by setting $h = 0$ in (3.16) and dividing by $m$ ($m \neq 0$). The result is

$$m_0 = \pm\{2(q\tilde{J})^{-1}[1 - (q\tilde{J})^{-1}]\}^{1/2}. \tag{3.25}$$

The spontaneous magnetization passes through a maximum value of $2^{-1/2}$ at $q\tilde{J} = 2$, and falls to zero as $\tilde{T} \to 0$ as well as at $\tilde{T}_c = q\tilde{J}/k$. [Equation (3.25) is that of an ellipse in the $m$, $qJ$ plane.]

The lack of convexity of $f(\tilde{J}, h)$ leads to no corresponding instability in the polymer problem. It results from the very different role played by $\tilde{J}$ and $h$ in the two interpretations of the model: In the magnet, $\tilde{J}$ and $h$ play the role of thermodynamic field variables, analogous to chemical potentials (strictly, to $\mu/kT$), while in the polymer problem they play a role analogous to activities $\exp(\mu/kT)$. As a ferromegnetic model the $n \to 0$ vector model is only a formal mathematical limit and need not have a thermodynamic interpretation in terms of $\tilde{J}$ and $h$, as field variables, while in terms of the polymer variables it is a *bona-fide* statistical mechanical model of a physical system. If the independent field variables $\ln\tilde{J}$ and $\ln h$ are used, then $f_0$ becomes the potential appropriate to the equilibrium polymerization model in terms of the variables $\Delta H_1/kT$ and $\Delta H_p/kT$, and convexity is restored.

The lack of convexity of $f(\tilde{J}, h)$ is not restricted to the limit $n \to 0$. It appears as soon as $n$ is less than 1. This is shown (for the molecular-field approximation) in Appendices A and C for the Hillhorst model and our model, respectively.

Although the failure of $f_0 = -\tilde{\phi}$ to satisfy convexity causes no problems when $\tilde{J}$ and $h$ are used as independent variables, caution must be used when changing independent variables. If one performs the "Legendre transform"

$$\tilde{\theta}(\tilde{J}, m) = \tilde{\phi} + hm \,, \tag{3.26}$$

with $h$ given by (3.16) or (3.18), the resulting free energy,

$$\tilde{\theta} = 1 \mp (1 - 2m^2)^{1/2} + \ln\{\tfrac{1}{2}[1 \pm (1 - 2m^2)^{1/2}\} - \tfrac{1}{2} q\tilde{J} m^2 \tag{3.27}$$

is double valued for all $\tilde{J}, m$, with the branch corresponding to the lower sign giving the lower free energy. This branch is nowhere convex in $m$. If the conventional free energy minimization procedures are applied, the (absurd) conclusion is reached that the system attains negatively infinite free energy by splitting into two "phases," one having infinite magnetic field, the other finite. The problem lies in the fact that although $\phi$ contains the same information whether viewed as a function of $h$ or $\ln h$, its Legendre transform possesses a totally different structure depending on the choice of independent variable. All of the original information is still present in $\tilde{\theta}(\tilde{J}, m)$, but it does not have a thermodynamic interpretation as a free energy.

Figure 1 shows the free energy $\tilde{\theta}$ as a function of $m$ for various values of $\tilde{J}$ corresponding to $\tilde{T} = 2\tilde{T}_c$, $\frac{1}{2}\tilde{T}_c$, and $\frac{1}{4}\tilde{T}_c$. Between $\tilde{T} = \tilde{T}_c$ and $\tilde{T} = \frac{1}{2}\tilde{T}_c$ the free energy exhibits a shallow minimum in the upper branch, corresponding to $h = 0$, at $m = m_0(\tilde{T})$ given by Eq. (3.26). At $\tilde{T} = \frac{1}{2}\tilde{T}_c$ the condition $h = 0$ is met at $m = 2^{-1/2}$, the maximum value of $m$. Below $\tilde{T} = \frac{1}{2}\tilde{T}_c$, $m_0(\tilde{T})$ is given by the local maximum in $\tilde{\theta}$ on the lower branch.

In Fig. 2 we show the regions in which $f_0 = -\tilde{\phi}$ does and does not satisfy convexity. The region in which convexity is satisfied is given by the inequality (3.17) and is indicated in Fig. 2 by shadowing.

## IV. PARTITION FUNCTION OF THE $n \to 0$ VECTOR MODEL

In this section we argue that Eq. (2.9) gives the partition function of the $n$-vector model in the $n \to 0$ limit. The average in (2.3) of the Hamiltonian in (2.1) can be expressed in the form

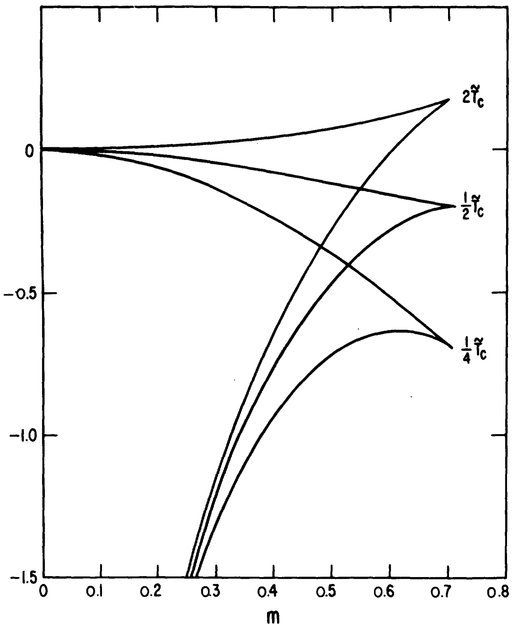

FIG. 1. The thermodynamic potential $\tilde{\theta}(\tilde{J}, m)$, defined by Eq. (3.27), as a function of $m$ for three values of $\tilde{T}$ in the molecular-field approximation.

$$Z = \left\langle \prod_{\langle i,j \rangle} \left(1 + \tilde{J}\vec{S}_1 \cdot \vec{S}_j + \frac{1}{2!}(\tilde{J}\vec{S}_1 \cdot \vec{S}_j)^2 + \cdots \right) \times \prod_i \left(1 + hS_i^{(1)} + \frac{1}{2!} h^2 (S_i^{(1)})^2 + \cdots \right) \right\rangle_{A^N} , \tag{4.1}$$

where the product $\Pi_i$ is over all sites and $\Pi_{\langle i,j \rangle}$ is over all distinct nearest-neighbor pairs of sites

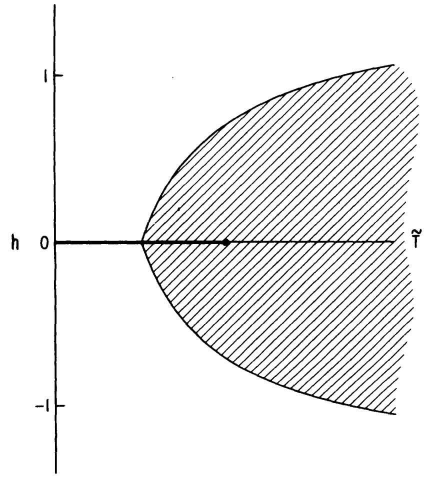

FIG. 2. Regions of convexity (shaded) and nonconvexity of $f(\tilde{J}, h)$ in the molecular-field approximation. Also shown is the coexistence curve (heavy line) and critical point. The region of convexity is given by Eq. (3.17).

and $+\cdots$ indicates the remaining terms in the Taylor series for the exponential function. Expanding out the products in (4.1) leads to a sum of averages of products of powers of spin components. Since the average $\langle\ \rangle_{AN}$ treats spins on distinct sites independently, only averages of the form

$$\left\langle \prod_\alpha (S_i^{(\alpha)})^{k_\alpha} \right\rangle_A \tag{4.2}$$

need to be calculated, where $\langle\ \rangle_A$ is defined by (2.4). The curious feature of the $n \to 0$ limit is that the only averages of the form (4.2) that survive are

$$\langle (S^{(\alpha)})^0 \rangle_A = \langle (S^{(\alpha)})^2 \rangle_A = 1\,. \tag{4.3}$$

This result may be obtained by the elegant generating function argument of Ref. 11. Alternatively, the angular averages may be evaluated explicitly in $n$ dimensions. The result (derived in Appendix B) is

$$\left\langle \prod_\alpha (S_i^{(\alpha)})^{2k_\alpha} \right\rangle_A = \left( \frac{\Gamma(\frac{1}{2}n)}{\Gamma(\frac{1}{2}n + \sum_\alpha k_\alpha)} \right) \left( \prod_\alpha \frac{\Gamma(k_\alpha + \frac{1}{2}) n^{k_\alpha}}{\Gamma(\frac{1}{2})} \right), \tag{4.4}$$

where $\Gamma(x)$ is the usual gamma function. [The average in (4.2) is zero if any $k_\alpha$ in (4.2) is odd.] If, for any particular choice of a set of $k_\alpha$, the right-hand side of (4.4) is evaluated as a function of $n$ and the formal limit $n \to 0$ is then taken, the result is that the only averages that do not vanish proportionally to some positive integer power of $n$ are those given in (4.3).

Because most of the averages in the expansion of (4.1) vanish, the sum is greatly simplified. Only a very limited number of kinds of products can possibly lead to a nonzero average. A simple non-self-intersecting closed loop arises from an appropriate product of terms $\tilde{J} S_i^\alpha S_j^\alpha$ ($i,j$ nearest neighbors), leading to a contribution, for an $l$-site loop,

$$\tilde{J}^l \prod_{i=1}^{l} \langle (S_i^\alpha)^2 \rangle_A = \tilde{J}^l\,. \tag{4.5}$$

If the loop were to cross itself there would result a higher power of $S_i^\alpha$ for some $i$ and the average would vanish as $n \to 0$. Unless $\alpha$ is the same in each factor $(\tilde{J} S_i^\alpha S_j^\alpha)$ there will appear an average of the form $\langle S_i^\alpha S_i^\beta \rangle_A$ that will vanish as $n \to 0$. Finally, there will be $n$ contributions of the form (4.5) (one from each value of $\alpha$) arising from the products $\vec{S}_i \cdot \vec{S}_j$ that produce it, so that the total weight of a closed loop (polymeric ring) of length $l$ will be $n\tilde{J}^l$. In the formal limit $n \to 0$ this vanishes, in agreement with the conclusions of Sarma. This same argument applies to the contributions from "two-site loops", of the form

$$\tfrac{1}{2} (\tilde{J} \vec{S}_i \cdot \vec{S}_j)^2\,, \tag{4.6}$$

which come from the second-order term in the first product in (4.1). All higher-order terms from this product also vanish as $n \to 0$.

A class of nonvanishing terms arises when a "chain" is initiated by a factor $hS_i^{(1)}$, then propagated by a set of factors $\tilde{J} S_i^{(1)} S_j^{(1)}$ and terminated by a factor $hS_j^{(1)}$. This leads to a contribution (for an $l$-site walk)

$$h^2 \tilde{J}^{(l-1)} \prod_{i=1}^{l} \langle (S_i^{(1)})^2 \rangle_A\,. \tag{4.7}$$

Each such walk of $b = l - 1$ bonds that does not intersect either itself or any other walk makes a contribution of

$$\tilde{J}^b h^2 \tag{4.8}$$

to the partition function. The second-order term in the second product in (4.1) can contribute nonvanishing single-site, zero-bond terms of the form

$$\tfrac{1}{2} h^2 \langle (S_i^{(1)})^2 \rangle_A = \tfrac{1}{2} h^2 (\tilde{J})^0 \tag{4.9}$$

provided no other chain visits site $i$. These terms appear to have been overlooked in the treatment in Ref. 11. They lead to nonvanishing contributions to the susceptibility in the $n \to 0$ limit that are accounted for in the treatment of Bowers and McKerrel.[12]

Examination of the possible contributions to (4.1) in the formal limit $n \to 0$ reveals that the mutually avoiding and self-avoiding walks (with single sites included) exhaust the nonvanishing contributions. The contribution of a single-site walk in (4.9) is of the same form as that of a two- or more-site walk in (4.8) except for the factor of $\frac{1}{2}$. The contribution from all nonvanishing averages can thus be expressed as the sum in Eq. (2.9).

The argument given above is in much the same style as that given by Sarma and is clearly quite informal. Its primary purpose is to show that if any expression of the form of our Eq. (2.9) or Sarma's[11(a)] Eq. (A19) gives the properties of the $n \to 0$ vector model correctly, then it must be our Eq. (2.9) rather than Sarma's Eq. (A19). This motivates the choice of the polymer statistical weights in (2.10) which leads to the partition function (2.12) for polymerization. It should be noted, however, that the use of an argument on the partition function $Z$ rather than on the limiting free energy per spin, $f = \lim_{N\to\infty} N^{-1} \ln Z$ amounts to an interchange of the usual order of the limits $N \to \infty$ and $n \to 0$. The free energy per spin obtained from taking the thermodynamic limit of the partition function in Eq. (2.9) is

$$f_1=\lim_{N\to\infty}\{N^{-1}\ln[\lim_{n\to 0}Z(n,N)]\},$$

whereas the usual convention would dictate the opposite order of limits:

$$f_2=\lim_{n\to 0}[\lim_{N\to\infty}N^{-1}\ln Z(n,N]\,.$$

There would seem to be no great difficulty in showing that the expansions of $f_1$ and $f_2$ in powers of $\tilde{J}$ and $h$ agree whenever $\tilde{J}$ and $h$ are sufficiently small that these expansions converge. In particular, we note that the zero-field high-temperature free energy and susceptibility series implied by Eq. (2.9) (i.e., obtained from $f_1$) are identical with those obtained by Bowers and McKerrel[12] (from $f_2$) when the difference in the normalization of magnetic field is accounted for. Series expansions for $f_2$ in powers of $\tilde{J}$ and $h$ are well known and much studied[17] for $n=1, 2, 3, \ldots$ and extrapolation of the results to $n=0$ gives answers in good agreement with direct counting estimates for polymers. On the other hand, our expression for $Z$ in Eq. (2.9) is valid at fixed $N$ and $n\to 0$ for *all* values of $\tilde{J}$ and $h$, and leads to a well-defined thermodynamic limit for $f_1(\tilde{J},h)$. By Eq. (2.12), this limiting free energy is necessarily intimately related to the properties of polymers and polymerization. Whether $f_2(\tilde{J},h)$ agrees with $f_1(\tilde{J},h)$ outside of the radius of convergence of its expansion in powers of $\tilde{J}$ and $h$ is a more difficult question.

In this regard it should be noted that the exact equivalence between the Tobolsky-Eisenberg theory of polymerization and the molecular-field approximation to the $n$-vector model of magnetism in the $n\to 0$ limit depends only upon the identification of variables in (3.20—(3.22) and not upon Eq. (2.9). [The identifications (3.20) and (3.21) together with Eq. (3.16) imply Eqs. (2.16) and (2.17).] Moreover, in obtaining the molecular-field approximation, the limit $N\to\infty$ is taken first and then the limit $n\to 0$, so that it is an approximation to $f_2$ that is obtained. The equivalence of this approximation in the limit $n\to 0$ with the Tobolsky-Eisenberg theory of polymerization (for *all* values of $\tilde{J}$ and $h$) suggests that the free energy $f_2$ of the $n\to 0$ vector model usefully describes polymers and polymerization even outside of the radius of convergence of $f_2$ in powers of $\tilde{J}$ and $h$, and thus suggests the identity of $f_1$ and $f_2$ for all $\tilde{J}$ and $h$. Proof of the identity of $f_1$ and $f_2$ throughout the $\tilde{J},h$ plane (or a counter proof) would be of considerable interest.

## V. DISCUSSION

The correspondence between a model of equilibrium polymerization (even though highly idealized) and the much studied $n$-vector model of ferromagnetism (even in the formal $n\to 0$ limit) provides an illuminating analogy that has been sought for some time. It has long been clear that the behavior of sulfur near 159 °C exhibits many features characteristic of critical phenomena,[18–20] and attempts have been made to analyze the behavior of sulfur in terms of the thermodynamics of phase transitions and critical phenomena.[21] On the other hand, it has also been clear[22] that sulfur is not likely to exhibit a mathematically sharp transition at 159 °C. The analogy of equilibrium polymerization with a magnet in a very small magnetic field makes it clear, in a particularly simple and familiar context, how equilibrium polymerization can fail to exhibit a mathematically sharp transition, yet still exhibit critical phenomena. The effect of a small magnetic field on the critical behavior of a magnet has been studied in some detail.[23]

The fact that the molecular-field approximation to the $n\to 0$ vector model is identical with the successful Tobolsky-Eisenberg theory of equilibrium polymerization lends confidence in the applicability of the $n\to 0$ vector model to equilibrium polymerization, and strongly suggests that the nonclassical critical behavior of the $n$-vector model will, in the formal $n\to 0$ limit, provide useful information about the deviations of liquid sulfur, and other monomer-polymer systems with very small $K_1$, from the classical TE theory.

The equivalence of the $n\to 0$ vector model with our model of equilibrium polymerization emphasizes certain limitations on the conventional interpretation[2,11] of the $n\to 0$ vector model in terms of nonreactive polymer solutions. The modifications implied by our corrected analysis do not by themselves present any serious difficulty. If $c_p$ and $c_m$ are the concentrations of polymers and of monomers in polymers, and if $\Pi$ is the osmotic pressure of the polymer solutions, then the identifications

$$\frac{\Pi v_0}{kT}=f\,, \tag{5.1}$$

$$2c_p=\frac{h}{v_0}\left(\frac{\partial f}{\partial h}\right)_{\tilde{J}}\,, \tag{5.2}$$

and

$$c_m-c_p=\frac{\tilde{J}}{v_0}\left(\frac{\partial f}{\partial \tilde{J}}\right)_h\,, \tag{5.3}$$

give the connection between the polymer solution and the $n$-vector model, where $v_0$ is the volume of a unit cell centered on the lattice site. These differ from the conventional treatment only in the replacement of $c_m$ by $c_m - c_p$ in Eq. (5.2). For polymers of high molecular weight, $c_m \gg c_p$ and this modification has virtually no effect. The interpretation of the model is now that sites, rather than bonds, are the monomers. The quantity $h^2$ plays the role of an activity of polymers, while $\tilde{J}$ is a parameter that, together with $h$, determines the average molecular weight. By adjusting $\tilde{J}$, the average molecular weight can be maintained constant while the concentration of polymers (and thereby the osmotic pressure $\Pi$) is varied.

According to the TE theory of equilibrium polymerization the molecular weights of the polymeric species are distributed exponentially. If $c_n$ is the concentration of polymers of length $n$, then according to TE,

$$v_0 c_n = \frac{K_1}{K_p}(K_p \phi_\lambda)^n \sim A e^{-bn}. \tag{5.4}$$

When the average molecular weight is very large, this implies a very small value of $b$, and a very broad, exponential distribution. While nonclassical critical behavior of the $n \to 0$ vector model may alter this mean-field prediction somewhat, it seems likely that the very broad distribution will persist. Thus, the $n \to 0$ vector model is not appropriate for describing solutions of polymers with molecular weight narrowly distributed about some large mean value. On the other hand, it may be quite appropriate for discussing solutions of polymers prepared by random termination, for which the molecular weight distribution is nearly exponential.[24]

The curiosity of the $n \to 0$ vector model noted in Sec. III—that $f(\tilde{J},h)$ is not everwhere convex—is not peculiar to the molecular-field approximation. We have recently shown[15] that if the $n \to 0$ vector model satisfies a scaling equation of state, then its free energy necessarily fails to satisfy the usual convexity requirements of thermodynamic stability, but the corresponding polymer problem exhibits no such instability in terms of polymer variables. Another example of this lack of convexity in the $n \to 0$ vector model is the negatively infinite susceptibility at the coexistence curve predicted by renormalization-group calculations,[25] and arising from the continuation to $n = 0$ of the effect of Goldstone modes at $n = 2$, 3, etc.

The diagram in Fig. 2 of the convex and nonconvex regions of $f$ is appropriate for the molecular-field approximation to the $n \to 0$ vector model. If the $n \to 0$ vector model exhibits nonclassical critical behavior (which seems very likely[26]) and is described by a scaling equation of state (which is more conjectural, but plausible), then we have shown[15] that $f(\tilde{J},h)$ fails to satisfy convexity even in the vicinity of the critical point. Based on that analysis it seems likely that the true boundary between convexity and nonconvexity of $f(\tilde{J},h)$ in the $n \to 0$ vector model is more nearly as shown in Fig. 3. Here the region of convexity of $f$ is a narrow wedge restricted to $\tilde{T} > \tilde{T}_c$ and bounded by the curves of the form

$$|h| \sim (\tilde{T} - \tilde{T}_c)^\Delta \tag{5.5}$$

with $\Delta$ given[26] approximately by 1.46.

The $n$-vector model exployed here and in Ref. 10 uses continuously variable vector spins of fixed length located at discrete lattice points in $d = 3$ dimensional space. This model may be generalized or altered in a variety of ways without affecting the essential results. Methods are well known[27] for replacing discrete spins by a spin density continuously variable in space by Fourier-transform techniques, and for replacing the constraint of fixed length spins with a distribution of spin lengths determined by a probability density. The formal $n \to 0$ limit of these models has long been employed in the study of polymers.[1,28,29] In the opposite direction, one can replace the continuously variable vector spin with a cubically symmetric discretely variable spin in $n$ spin dimensions and, following Hillhorst,[13] take the formal $n \to 0$ limit to obtain information about polymers. It is shown in Appendix A that the mean-field approximation to this discrete vector model also becomes identical to the Tobolsky-Eisenberg theory in the $n \to 0$ limit. This suggests that real-space renormalization-group calculations of the critical properties of this discrete $n \to 0$ vector model, such as those carried out by Hillhorst,[13] but in three spatial dimensions, may be useful in describing the critical behavior ob-

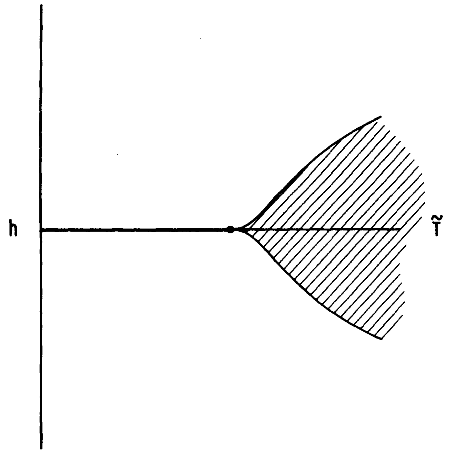

FIG. 3. Regions of convexity (shaded) and nonconvexity of $f(\tilde{J},h)$ if scaling is obeyed at the critical point. The boundary is given by Eq. (5.5).

served in equilibrium polymerization. We are currently pursuing this possibility.

The model can be generalized in other ways. We have examined[30] a dilute $n$-vector model in the $n \to 0$ limit and shown that it is equivalent to a model for equilibrium polymerization in a solvent. In the molecular-field approximation it becomes identical to the earlier theory of Scott[31] for the phase equilibria in liquid sulfur solutions. According to this model, the lower critical solution temperature observed in certain sulfur solutions is intimately associated with the tricritical point found in models for dilute magnets, metamagnets in a field, and $^3$He-$^4$He mixtures.

It seems likely that still other useful generalizations remain to be discovered. Inclusion of the possibility of cross linking between polymers may provide a connection with the theories of gels and percolation which have been the focus of much interest recently.[32]

*Note added in proof.* P. D. Gujrati [Phys. Rev. B (to be published); Phys. Rev. A (to be published)] has apparently independently discovered the error in the earlier analysis (Ref. 11) of the $n \to 0$ vector model. Gujrati gives the corrected partition function in a form that is different from but equivalent to ours. His transcription to the polymer problem appears quite different from ours but this is due simply to a different interpretation of the polymer problem. He counts as polymers only those objects that would in our model be called dimers, trimers, tetramers, etc. Either interpretation seems acceptable as a description of polymer solutions, and the two descriptions become indistinguishable from each other (and from the earlier treatment in Ref. 11) in the limit of very dilute solutions of very high molecular weight polymers.

## ACKNOWLEDGMENT

This research was supported by the National Science Foundation through Grant No. CHE 78-25188. The hospitality of Muir College to Pierre Pfeuty during the completion of this work is gratefully acknowledged.

## APPENDIX A: THE HILLHORST MODEL AND EQUILIBRIUM POLYMERIZATION

Consider a system of $N$ cubically $n$-component discrete spins $\vec{\sigma}_i$ located on the sites of a regular $d=3$ dimensional lattice and interacting through the Hamiltonian

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} \vec{\sigma}_i \cdot \vec{\sigma}_j - m_0 H \sum_i \sigma_i^{(1)} , \tag{A1}$$

where the sums $\sum_i$ and $\sum_{\langle i,j \rangle}$ are over all sites and all distinct nearest-neighbor pairs $\langle i,j \rangle$ of sites and $\vec{\sigma}_i$ is a cubically discrete $n$-component spin of norm $\sqrt{n}$, that is, $\vec{\sigma}_i = (0,0,\ldots,\pm n^{1/2},\ldots,0)$, which can point in any of $2n$ directions.

We define the partition function and free energy of this model as

$$Z = e^{Nf} = (2n)^{-N} \sum_{\{\vec{\sigma}_i\}} \exp(\mathcal{H}/kT) . \tag{A2}$$

Following Hillhorst[13] it is easy to show that the partition function $Z$ in (A2) is given, in the limit $n \to 0$, by expression (2.9) for the $n \to 0$ continuous $n$-vector model. The two models are equivalent in both limits $n \to 0$ and $n=1$. We shall now treat this model in the molecular-field approximation and show that we again recover the Tobolsky-Eisenberg theory.

In the nonzero field $H$, the average value of $\sigma_i^\alpha$ is given by $\langle \sigma_i^1 \rangle = m \neq 0$ and $\langle \sigma_i^\alpha \rangle = 0$ if $\alpha \neq 1$. The molecular-field approximation is equivalent to replacing the Hamiltonian in (A1) by the Hamiltonian

$$\mathcal{H}_0 = \sum_i (qJm + m_0 H)\sigma_i^1 + \tfrac{1}{2} q m^2 N J . \tag{A3}$$

The constant term in (A3) is chosen so that the mean total energy is equal to $E_0 = -N(\frac{1}{2} qJm^2 + m_0 m H)$. Performing the sum over all possible spin configurations we obtain, for the magnetization,

$$\begin{aligned} m &= \frac{1}{Z} (2n)^{-N} \sum_{\{\vec{\sigma}_i\}} \sigma_i^{(1)} \exp(-\mathcal{H}/k\tilde{T}) \\ &= \frac{\sqrt{n}\ \sinh[\sqrt{n}(q\tilde{J}m + h)]}{n - 1 + \cosh[\sqrt{n}(q\tilde{J}m + h)]} , \end{aligned} \tag{A4}$$

where $\tilde{J} = J/k\tilde{T}$ and $h = m_0 H/k\tilde{T}$. Similarly, we obtain

$$\begin{aligned} -f &= \tilde{\phi} \\ &= \tfrac{1}{2} q\tilde{J}m^2 - \ln\{(n-1) + \cosh[\sqrt{n}(q\tilde{J}m + h)]\} , \\ e &= \left( \frac{\partial f}{\partial \tilde{J}} \right)_h = \tfrac{1}{2} q m^2 . \end{aligned} \tag{A5}$$

These results can also be obtained by the minimization procedure used in Sec. III. Expressions (A4) and (A5) are valid for all values of $n$. In the limit $n \to 0$ we recover expressions (3.13)–(3.15) already obtained for the molecular-field theory of the $n \to 0$ vector model.

From expression (A4) we see that the spontaneous magnetization in the zero field is anomalous as soon as $n < 1$: As $\tilde{T}$ goes from zero to $\tilde{T}_c$ the magnetization starts at $\sqrt{n}$, increases to maximum, and then decreases to reach zero at $\tilde{T}_c$. When $q\tilde{J}m + h$ is large (either $h \to \infty$ or $\tilde{T} \to 0$), then

$$m = n^{1/2}\{1 + 2(1-n)\exp[-n(q\bar{J}m + h)] + \cdots\}. \quad \text{(A6)}$$

This shows that $m$ increases when $T$ increases and that $m$ decreases when $h$ increases so that the susceptibility is negative for a sufficiently high field.

## APPENDIX B: ANGULAR AVERAGES IN $n$ DIMENSIONS

A vector of length $\sqrt{n}$ in $n$ dimensions can be represented by polar coordinates in the form

$$\begin{aligned}
S^{(1)} &= \sqrt{n}\,\cos\theta_1,\\
S^{(2)} &= \sqrt{n}\,\sin\theta_1\cos\theta_2,\\
S^{(3)} &= \sqrt{n}\,\sin\theta_1\sin\theta_2\cos\theta_3,\\
&\;\;\cdot\\
&\;\;\cdot\\
&\;\;\cdot\\
S^{(n-1)} &= \sqrt{n}\,\sin\theta_1\sin\theta_2\cdots\sin\theta_{n-2}\cos\theta_{n-1},\\
S^{(n)} &= \sqrt{n}\,\sin\theta_1\sin\theta_2\cdots\sin\theta_{n-2}\sin\theta_{n-1}.
\end{aligned} \quad \text{(B1)}$$

The integration over all solid angles takes the form

$$\int d\Omega^{(n)}(\cdot) = \int_0^\pi d\theta_1 \int_0^\pi d\theta_2 \cdots \int_0^\pi d\theta_{n-2} \int_0^{2\pi} d\theta_{n-1} (\sin\theta_1)^{n-2}(\sin\theta_2)^{n-3}\cdots(\sin\theta_{n-2})(\cdot). \quad \text{(B2)}$$

It is readily verified by direct integration that this gives

$$A_n = \int d\Omega_1^{(n)} = \frac{2\pi^{n/2}}{\Gamma(n/2)}. \quad \text{(B3)}$$

Evaluation for integer $n$ gives $A_1 = 2$, $A_2 = 2\pi$, $A_3 = 4\pi$, etc. It is interesting that (A3) not only reproduces the familiar results in two and three dimensions, but also the correct $n=1$ result: $\sum_{\pm 1} 1 = 2$. As $n \to 0$ it gives the formal limit $A_n \sim n$.

Inspection of the form (B2) shows that the average in (3.10) can be written in the form

$$\begin{aligned}
\langle (S^{(1)})^{2k}\rangle_A = n^k \langle (\cos\theta_1)^{2k}\rangle_A &= n^k \frac{\int_0^\pi (\cos\theta_1)^{2k}(\sin\theta_1)^{n-2}d\theta_1}{\int_0^\pi (\sin\theta_1)^{n-2}d\theta_1}\\
&= n^k B\left(\frac{2k+1}{2}, \frac{n-1}{2}\right) \Big/ B\left(\frac{1}{2}, \frac{n-1}{2}\right),
\end{aligned} \quad \text{(B4)}$$

where $B(x,y)$ is the standard beta function

$$\begin{aligned}
B(x,y) &= 2\int_0^{(1/2)\pi} \sin^{2x-1}\phi\,\cos^{2y-1}\phi\,d\phi\\
&= \Gamma(x)\Gamma(y)/\Gamma(x+y).
\end{aligned} \quad \text{(B5)}$$

Evaluation of (B4) using (B5) and the properties of the gamma function gives (3.10).

Equation (4.4) may be obtained by using (B1) to express $\prod_\alpha (S^{(\alpha)})^{2k_\alpha}$ in terms of $\theta_1 \cdots \theta_{n-1}$ and $n$ and then evaluating the resulting average in the manner of (B4). The result is

$$\begin{aligned}
\left\langle \prod_\alpha (S^{(\alpha)})^{2k_\alpha} \right\rangle &= (n^{\Sigma k_\alpha}) \prod_{\alpha=1}^{n-1} \left( \frac{\int_0^\pi (\sin\theta_\alpha)^{(n-\alpha-1+2k_{\alpha+1}+\cdots+2k_n)}(\cos\theta_\alpha)^{2k_\alpha}d\theta_\alpha}{\int_0^\pi (\sin\theta_\alpha)^{n-\alpha-1}} \right)\\
&= (n^{\Sigma k_\alpha}) \prod_{\alpha=1}^{n-1} \left( \frac{B\left(\frac{n-\alpha}{2} + \sum_{\beta=\alpha+1}^{n} k_\beta,\ \frac{1}{2}+k_\alpha\right)}{B\left(\frac{n-\alpha}{2}, \frac{1}{2}\right)} \right).
\end{aligned} \quad \text{(B6)}$$

Inserting the expression for $B(x,y)$ in terms of gamma functions in (B5) and canceling common terms in the numerator and denominator gives (4.4).

## APPENDIX C: MEAN-FIELD $n$-VECTOR MODEL FOR GENERAL $n$

The magnetization of the $n$-vector model in the molecular-field approximation can be expressed (cf. Appendix B) in the form

$$\begin{aligned}
m &= \frac{\int d\Omega^{(n)} \exp[(q\bar{J}m + h)\sqrt{n}\cos\theta]\sqrt{n}\cos\theta}{\int d\Omega^{(n)} \exp[(q\bar{J}m + h)\sqrt{n}\cos\theta]}\\
&= \frac{\int_0^\pi \exp[(q\bar{J}m + h)\sqrt{n}\cos\theta]\sqrt{n}\cos\theta(\sin\theta)^{n-2}d\theta}{\int_0^\pi \exp[(q\bar{J}m + h)\sqrt{n}\cos\theta](\sin\theta)^{n-2}d\theta}.
\end{aligned} \quad \text{(C1)}$$

Using standard identities for Bessel functions we have

$$f_1(z) \equiv \int_0^\pi e^{z\cos\theta} \sin^{2\nu}\theta \, d\theta = \Gamma(\nu + \tfrac{1}{2})\Gamma(\tfrac{1}{2})(\tfrac{1}{2}z)^{-\nu} I_\nu(z) , \tag{C2}$$

$$\begin{aligned} f_2(x) &\equiv \int_0^\pi e^{z\cos\theta} \sin^{2\nu}\theta \cos\theta \, d\theta = f_1'(z) \\ &= \Gamma(\nu + \tfrac{1}{2})\,\Gamma(\tfrac{1}{2})(\tfrac{1}{2}z)^{-\nu}\left(I_\nu'(z) - \frac{\nu}{z} I_\nu(z)\right) \\ &= \Gamma(\nu + \tfrac{1}{2})\Gamma(\tfrac{1}{2})(\tfrac{1}{2}z)^{-\nu} I_{\nu+1}(z) , \end{aligned}$$

where the prime denotes differentiation with respect to $z$, and $I_\nu$ is the Bessel function given by

$$I_\nu(z) = (\tfrac{1}{2}z)^\nu \sum_{k=0}^{\infty} \frac{(\frac{1}{4}z^2)^k}{k!\,\Gamma(\nu + k + 1)} . \tag{C3}$$

Combining the results in (C2) we have

$$m = \frac{\sqrt{n}\, I_{n/2}[\sqrt{n}\,(q\tilde{J}m + h)]}{I_{n/2-1}[\sqrt{n}\,(q\tilde{J}m + h)]} . \tag{C4}$$

For $n = 1$, standard expressions for $I_{\pm 1/2}$ give

$$m = \tanh(qJm + h) ,$$

the usual result for the Ising model. Using the expansion in (C3) for nonzero $n$ in the numerator and denominator of (C4) and then letting $n \to 0$, we obtain (3.14).

In a similar fashion we obtain for $\mathrm{Tr}(e^{-\beta h_1})$ in (3.9),

$$\mathrm{Tr}\, e^{-\beta h_1} = \Gamma(\tfrac{1}{2}n) \frac{I_{n/2-1}[\sqrt{n}\,(q\tilde{J}m + h)]}{[\frac{1}{2}\sqrt{n}\,(q\tilde{J}n + h)]^{n/2-1}} . \tag{C5}$$

This may be combined with (3.8) to give $\tilde{\phi}$. In the limit $n \to 0$, (3.12) is recovered for $\mathrm{Tr}\, e^{-\beta h_1}$ and so (3.13) for $\tilde{\phi}$. The result (3.15) for $e$ is an identity for all $n$ in the molecular-field approximation.

The failure of $f(\tilde{J}, h)$ to be convex arises immediately below $n = 1$, as in the discrete case (cf. Appendix A). To see this, consider (C4) when $(qJm + h)$ is large (either because $h$ is large or because $\tilde{J}$ is large) and $n$ is fixed. The asymptotic expression

$$I_\nu(z) \sim \frac{e^z}{(2\pi z)^{1/2}} \left(1 - \frac{\mu - 1}{8z} + \frac{(\mu - 1)(\mu - 9)}{2!(8z)^2} + \cdots\right) \tag{C6}$$

for large $z$, where $\mu = 4\nu^2$, gives for $m$,

$$m \sim \sqrt{n}\left[1 + \frac{(1 - n)}{2\sqrt{n}(q\tilde{J}m + h)} + O\left(\frac{1}{(q\tilde{J}m + h)}\right)^2\right] . \tag{C7}$$

For $h$ very large at fixed $T$, the magnetization approaches $\sqrt{n}$ and is a decreasing function of $h$ as $h \to \infty$. For $h = 0$ the spontaneous magnetization approaches $\sqrt{n}$ as $\tilde{T} \to 0$ and is an increasing function of $\tilde{T}$ near $\tilde{T} = 0$.

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