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Equilibrium polymerization of chains and rings: A bicritical phenomenon

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The equilibrium polymerization of chains and rings together is a $(n=1)$ critical phenomenon with aspects of *bicriticality*, governed by exponents not found in any symmetric $O(n)$ model. The bicritical nature of the critical point is the result of a competition between a transition to form long-chain polymers and a transition to form an infinite-rings condensate. As a result the fraction of monomers incorporated in chains and in rings varies with temperature according to a different power law than that for the total fraction of polymerized material and is governed by an exponent that depends on the crossover exponent ϕ for quadratic anisotropy for the $O(n)$ vector model of magnetism in the limit $n \rightarrow 1$. Moreover, the fraction of monomers in polymeric rings is found to decrease with temperature with infinite slope just beyond the transition in the polymerized phase. Similarly, the geometry of large polymers is described by a power law $R \sim N^{\nu/\phi}$, where R is the distance spanned by a polymer segment of N monomers and where the exponent is not the de Gennes result $\nu(n=0)$ for chains alone, but rather also depends on the crossover exponent ϕ for $n=1$. We study the equilibrium polymerization of chains and rings together using a variety of techniques, including simple equilibrium theory, a lattice model, field-theoretic correspondence to magnetism and a direct renormalization-group calculation on a polymer model. An explicit parametric form for the equation of state is presented to lowest order in ϵ. Results are obtained for the fraction of polymeric material in chains and rings and for various correlation functions of interest in considering the geometry and distribution of chains and rings.

I. INTRODUCTION

The autoassembly of monomers to form large linear polymers under conditions approximating chemical equilibrium is a very general phenomenon found widely in nature. In pure liquid sulfur and dilute liquid sulfur solutions high-molecular-weight polymers form from monomeric S_8 rings at a sharp transition temperature at which well-documented critical anomalies occur.[1-5] An analogous transition occurs in the formation of "living polymers,"[6] notably poly-α-methylstyrene[7] and polytetrahydrofuran.[8] Under appropriate conditions long linear polymerlike micelles can form from surfactant molecules in solution.[9] In the biological realm actin and tubulin filaments[10] polymerize from protein subunits to form the skeleton of the living cell. Such phenomena also exist in lower dimensions. In two dimensions the commensurate-incommensurate transition in adsorbed monolayers can be described by the appearance of domain walls[11] that behave in many ways like equilibrium linear polymeric structures. In one dimension many phenomena such as the helix-coil transition[12] can be described as an equilibrium polymerization.

Simple equilibrium theories of polymerization of chains and of chains and rings have existed for many years. Gee[13,14] and Tobolsky and Eisenberg[15] developed a theory for the polymerization of sulfur chain polymers from S_8 monomers. This was later generalized to deal with "living" polymers.[16] Scott[17] generalized the Tobolsky-Eisenberg theory to solutions of sulfur in an inert solvent and first showed explicitly that it followed from the Flory[18] theory of polymer solutions. An almost identical theory was developed by Oosawa[19] to describe the autoassembly of protein subunits to form actin and similar filaments, and similar ideas have been used to describe the formation of polymeric micelles.[20] These theories can be thought of as governed by two equilibrium constants, an "initiation" equilibrium constant K_1 for the activation of a monomer (for the opening of a S_8 ring to form a diradical S_8 chain in the case of sulfur) and a "propagation" equilibrium constant K_p for the growth of the chain by addition of one inactive monomer (a S_8 ring in sulfur). There is a mathematically sharp phase transition only in the limit $K_1 \rightarrow 0$. The very small value of K_1 in sulfur ($K_1 \cong 10^{-12}$) explains the experimental sharpness of the transition there. The transition occurs at a value of K_p of order unity (exactly at $K_p = 1$ for the Tobolsky-Eisenberg theory). Corresponding chemical equilibrium theories for the simultaneous equilibrium polymerization of chains and polymeric rings were considered for the case of sulfur, first by Fairbrother, Gee, and Merrall,[14] and later in more detail by Harris.[21] Polymeric chain, polymeric ring equilibrium was also studied in a more general context by Jacobsen and Stockmayer,[22] and the same ideas have recently been employed in treatment of polymeric micelles by Porte.[23] The "conventional wisdom" emanating from all of these studies is that polymeric rings play only a minor role in the transition and are dominated by the polymeric chains, once these form, because of the entropic cost of closing a chain to form a ring.

Recently we have shown[24–31] that the equilibrium polymerization of monomers to form long polymeric chains is described by the $n \to 0$ limit of the n-vector model of magnetism, and is thus a critical phenomenon described by nonclassical critical exponents. In this correspondence the magnetic field (divided by temperature) h plays a role analogous to a Boltzmann factor for the chain ends, i.e., to the square root of the initiation equilibrium constant K_1, and the coupling constant between spins divided by temperature, $\tilde{J}$, plays a role analogous to the propagation constant K_p of Tobolsky-Eisenberg theory, i.e.,

$$\begin{aligned} &h \sim \sqrt{K_1}\ , \\ &\tilde{J} \sim K_p\ . \end{aligned} \tag{1.1}$$

This correspondence allows the powerful machinery developed over the last 20 years for the study of phase transitions and critical phenomena[32–37] to be brought to bear on the phenomenon of equilibrium polymerization. We showed[25] that in the mean-field approximation the $n \to 0$ vector model reduces *identically* to the Tobolsky-Eisenberg (TE) theory of equilibrium polymerization throughout the h,T plane (K_1,K_p plane). Thus, the transition is, within TE theory, an Ehrenfest second-order transition, and nonclassical critical behavior is to be expected due to fluctuations ignored in mean-field theory.

The use of renormalization-group estimates for critical exponents of the $n \to 0$ vector model and a simple scaling-law equation of state has been remarkably successful in describing the anomalies in pure and doped sulfur[24,28,29,31] and in living polymers,[27] and mean-field approximation to a corresponding dilute $n \to 0$ vector model for sulfur solutions has proven very useful in elucidating the possible phase diagrams in these systems.[26,38] This work builds upon the pioneering studies by de Gennes[39] and des Cloiseaux[40] of the statistical mechanics of simple polymers and nonreactive polymer solutions in terms of the $n \to 0$ vector model. Gujrati[41] has also considered various aspects of the $n \to 0$ and related models.

Shortly after the appearance of Ref. 24 it was argued by Cordery[42] that if polymeric rings are included in the equilibrium then the appropriate universality class of the critical phenomena is that of the Ising model ($n=1$) rather than $n=0$. Several other authors[43–47] argued in independent ways that the appropriate universality class for polymeric rings and chains in equilibrium was that of the n-vector model with $n>0$, but as noted by Duplantier and Pfeuty[45] and argued explicitly below, if the breaking of a bond in the middle of a very large ring is chemically equivalent to the breaking of a bond in a very long chain, then the appropriate universality class is $n=1$, as argued by Cordery.

From one point of view, this change in universality class is not crucial. The connection with nonclassical critical phenomena and the advantage of a map to a model of magnetism remain. Moreover, the identification of the magnetic field of the magnet with the statistical weight of an end of a polymer chain remains the same in the limit $h \to 0$, the limit relevant to critical phenomena. On the other hand, the change in universality class from $n=0$ to $n=1$ results in a change in the value of α, the exponent governing the specific heat anomaly, by a factor of 2 from $\alpha \cong 0.24$ for $n=0$ to $\alpha \cong 0.12$ for $n=1$. Moreover, any change in universality class can result from the presence of rings only if rings of arbitrarily large size are present. This leads to the question as to whether chains really play an important role at all, especially in the limit $K_1 \to 0$, where the concentration of chain ends (and therefore the number concentration of chains) tends to zero. Indeed, one could easily conclude from Cordery's treatment that only rings are present in the limit $K_1 \to 0$. While this is certainly true for $\tilde{J} < \tilde{J}_c$, it is by no means obvious for $\tilde{J} > \tilde{J}_c$. Experimental results and comparison with the classical TE and nonclassical $n \to 0$ vector model theories suggest[29] that a non-negligible fraction of the sulfur must be incorporated in chains when $\tilde{J} > \tilde{J}_c$. With the existing theories, however, it was only possible to determine the total amount of polymeric materials, rings plus chains, and not the fraction of monomers incorporated in chains or rings separately.

Recently we have found[48] that the polymerization transition of chains and rings together has an aspect of bicriticality. Quadratic anisotropy is introduced to break the symmetry inherent in the physical requirement that the propagation constant be the same for very large polymeric rings and chains. This allows the separate determination of the fraction of monomers incorporated in polymeric rings and chains. Several interesting consequences follow.

First, the fraction of monomers in chains is described by a new critical exponent, not found in the symmetric O(n) vector model, and related to the crossover exponent, ϕ, for quadratic anisotropy.[49] While the total fraction of monomers in polymers of all kinds is given by

$$\phi_{\text{tot}} = \phi_{\text{tot}}^{c} + A(\tilde{J}-\tilde{J}_c) + B_{\pm}(\tilde{J}-\tilde{J}_c)^{1-\alpha}\ , \tag{1.2}$$

where α is the specific-heat exponent of the $n \to 1$ vector model, the fraction of monomers in chains ϕ_c is given by

$$\phi_c \sim B_c(\tilde{J}-\tilde{J}_c)^{2-\alpha-\phi} \quad (\tilde{J} > J_c)\ . \tag{1.3}$$

For $\tilde{J} > \tilde{J}_c$ when $h \to 0$, where ϕ is the crossover exponent for quadratic anisotropy in the limit $n \to 1$.

Second, because ϕ is greater than unity for $n>0$ ($\alpha \approx 0.12$, $\phi \approx 1.08$, for $n=1$ in three dimensions),[49,50] the fraction of monomers in chains grows more rapidly above $\tilde{J}_c$ than does the total fraction in polymers. This growth occurs at the expense of rings, the fraction of monomers in which must decrease with infinite slope just above $\tilde{J}_c$.

Third, the physical transition point is the result of a delicate balance between two quite different kinds of polymerization, a transition to a state with a very flat, polydisperse distribution of chains of very high average molecular weight, and a quite different transition to a state with an "infinite-ring condensate" of polymeric rings with radius of gyration bounded only by the size of the container.

Fourth, the crossover exponent ϕ also plays an interesting role in the description of the geometry or "fractal dimensionality" of large polymers on a distance scale short compared to the correlation length, i.e., short compared to the distance scale on which a large polymer meets other large polymers. As first pointed out by de Gennes,[39] for an isolated polymer chain in a good solvent, the number of monomers N required to span a distance R varies as

$$N \sim R^D \tag{1.4}$$

as $R \rightarrow \infty$, where the fractal dimensionality D is given by

$$D = 1/\nu \quad (n = 0) , \tag{1.5}$$

and ν is the critical exponent describing the divergence of the correlation length of the $n \rightarrow 0$ vector model. The same result holds in the case of equilibrium polymerization of chains provided R is short compared to the correlation length as well as large compared to the size of monomers. When rings are also in equilibrium, however, the correct result is neither $D = 1/\nu$ for $n = 0$ nor $D = 1/\nu$ for $n = 1$, but rather

$$D = \phi/\nu \quad (n = 1) . \tag{1.6}$$

In fact, the result for chains alone can be thought of as (1.6) with $n = 0$ rather than (1.5), because $\phi \rightarrow 1$ as $n \rightarrow 0$ independent of dimensionality. This result was presented earlier using a simple scaling argument.[51]

In this paper we develop in more detail the results presented in our letters[48,51] and obtain a number of new results. In Sec. II we give a more detailed analysis, for general spatial dimension d, of the simple chemical equilibrium theory presented in our letter. We give there the arguments concerning the nature of the ring condensate and note that the theory leads to "nonclassical" critical exponents identical to those of the spherical model. A more detailed treatment of a random-walk model which leads to the same asymptotic results as those in Sec. II is presented in Appendix A. In Sec. III we demonstrate an exact correspondence between a plausible lattice model of equilibrium polymerization of chains and rings and an n-vector model of magnetism and show that incorporation of quadratic anisotropy in the Hamiltonian of the magnetic model allows the evaluation of the fraction of monomers incorporated in chain or ring polymers separately. The model of polymerization is essentially that of Cordery. The magnetic model is a fixed-length classical n-vector model on a lattice similar in spirit to that used recently by Nienhuis.[52] In the limit of zero magnetic and anisotropy fields (the limit of interest) it has the same symmetry as the O(n) vector model and retains this symmetry to lowest order in an expansion in powers of these fields. We use this correspondence to obtain the exponents and scaling behavior of the fraction of monomers incorporated in chains and rings as well as the total fraction of polymerized material. We also present in this section the argument that if the breaking of a bond in a very large chain is chemically identical to that in a very large ring, then the appropriate value of n for the n-vector model is $n = 1$ for polymeric rings without a sense of direction (e.g., for sulfur).

In Sec. IV we present a simple continuum model for the equilibrium polymerization of chains and rings with excluded volume and carry out a direct renormalization-group calculation of its properties to first order in $\epsilon = 4 - d$. While the methods employed in the renormalization-group calculation are essentially identical to those employed in field-theoretic calculations on magnetic systems, we make no direct use in this section of any map to a magnetic model. This has the advantage that certain generalizations are possible that are not at all natural within the magnetic analogy. For example, it is possible to consider the case in which the propagation equilibrium constant for chains, K_c, is different from that of rings, K_r, and thus to examine the nature of the ring condensate of Sec. II when there are excluded volume effects. The values of the exponents obtained by this treatment are identical (to the order in ϵ calculated) with those for the n-vector model with $n = 1$, confirming the correspondence obtained in Ref. 48, and in Secs. III and V and Appendix B of this paper.

In our letter[48] we outlined a correspondence between a field-theoretic model of chains and rings in equilibrium and the field theory of magnetism for the n-vector model with quadratic anisotropy. In Sec. V we use this correspondence to extract the expected scaling behavior of various densities and correlation functions. In particular, we obtain the result in Eq. (1.3) for the exponent governing ϕ_c and extract the scaling function to lowest order in ϵ. We use more general quadratic anisotropy operators to extract the result in Eq. (1.6) and to discuss the length distribution of long chains in the polymerized regime, the possibility of considering $K_c \neq K_r$ in the magnetic analogy, and the crossover from chains to ring condensate. A more detailed presentation of the correspondence between the field theory of magnetism and that of equilibrium polymerization of chains and rings is given in Appendix B, where attention is given to the terms in the perturbation expansion of the magnet generated by higher-order terms in the Ursell-Mayer expansion of the two-body repulsive interaction between monomers in the polymers.

Our result concerning the Hausdorff dimension embodied in Eq. (1.4) with Eq. (1.6) is derived in two different ways in Secs. IV and V. In Sec. IV we obtain Eq. (1.4) with a direct renormalization-group calculation of D to first order in ϵ without recourse to any magnetic analogy. In Sec. V we obtain the relation (1.6) by formal comparison of magnetic correlation functions with the corresponding polymer averages. A similar derivation could be carried out in Sec. III. The agreement to first order in ϵ of the exponent D obtained in Sec. IV with the known[49,50] ϵ expansion for ϕ/ν provides an additional confirmation of the usefulness of the magnetic analogy. A discussion of the results and indications of areas for further work are contained in Sec. VI.

II. CHEMICAL EQUILIBRIUM THEORY

In this section we develop in more detail a simple chemical equilibrium theory of equilibrium polymerization of chains and rings that was described briefly in Ref.

48. Let x_{mc} and x_{mr} be the number of chains and rings, respectively, of m monomers divided by the total number of monomers, both free and in polymers. They are taken to be related to the fraction, x_0, of free monomers by the relations

$$x_{mc}=K_1x_0(K_cx_0)^{m-1} \quad (m\geq 1)\ ,$$

$$x_{mr}=Bm^{-(d/2+1)}(K_rx_0)^m \quad (m\geq 2)\ , \tag{2.1}$$

where d is the spatial dimensionality. We are, of course, primarily interested in $d=3$, but it will be illuminating to treat d as a variable parameter and to consider the behavior of the model for $2<d<4$. The constant K_1 is a statistical weight associated with the chain ends, and may be interpreted as the equilibrium constant for activation of a monomer (e.g., opening of a S_8 ring). The constants K_c and K_r are statistical weights associated with bonds between monomers that include an estimate (per bond) of the number of ways to place a chain on a lattice. Equation (2.1) amounts to a choice of the equilibrium constant for adding one inactive monomer to a chain or ring of length m.

The choice of x_{mc} is essentially that employed by Gee[13] and Tobolsky and Eisenberg.[15] The factor $Bm^{-d/2}$ in x_{mr} accounts for the ratio of closed loops to open chains for random walks in the limit of large m in d spatial dimensions, while the additional factor of m^{-1} accounts for the fact that a ring may be formed by chain closure at any of its m bonds. The constant B depends upon the details of the walk, in particular upon the rigidity of the monomer units, and may therefore be viewed as an adjustable parameter in the theory. The use of Eq. (2.1) for x_{mr} for small m constitutes an arbitrary choice of ring propagation constant for small m. Harris[21] and Jacobsen and Stockmayer[22] have considered models for chain and ring polymerization based on similar ideas. The novel feature of the model in Eq. (2.1) is that we allow, at least formally, for the possibility that the chain and ring propagation constants, K_c and K_r are unequal. Physically, we expect that K_c must equal K_r at least for very large m, so that if K_c and K_r are to be taken independent of m, they must be taken equal for all m. However, it is often useful in studying physical systems to consider an enlarged parameter space in which certain physical symmetries are broken and in which the system of interest lies on some special locus. That point of view turns out to be fruitful here as well.

The total numbers of chains and rings, respectively, divided by the total number of monomers are given by

$$x_c\equiv\sum_{m=1}^{\infty}x_{mc}=K_1x_0/(1-K_cx_0)\ ,$$

$$x_r\equiv\sum_{m=2}^{\infty}x_{mr}=B[\Phi(K_rx_0,\tfrac{1}{2}d+1)-1]K_rx_0\ , \tag{2.2}$$

and the fractions of monomers incorporated in chains and rings are given by

$$\phi_c=\sum_{m=1}^{\infty}mx_{mc}=K_1x_0/(1-K_cx_0)^2\ ,$$

$$\phi_r=\sum_{m=2}^{\infty}mx_{mr}=B[\Phi(K_rx_0,\tfrac{1}{2}d)-1]K_rx_0\ , \tag{2.3}$$

where

$$\Phi(z,s)\equiv\sum_{n=0}^{\infty}(n+1)^{-s}z^n \tag{2.4}$$

is a function the properties of which are well known.[53] In particular, $\Phi(z,s)$ has a branch-point singularity at $z=1$ and possesses the expansion about $z=1$ of the form[53]

$$z\Phi(z,s)=\Gamma(1-s)[\ln(1/z)]^{s-1}$$

$$+\sum_{r=0}^{\infty}\frac{2\Gamma(r+1-s)}{(2\pi)^{1-s}r!}\sin[\pi(s-r)/2]$$

$$\times\zeta(r+1-s)\left[\frac{\ln(z)}{2\pi}\right]^r\ , \tag{2.5}$$

where $\Gamma(x)$ is the gamma function and $\zeta(x)$ is the Riemann zeta function, defined by analytic continuation and finite everywhere except $x=1$. Thus, x_r and ϕ_r are both well-defined and finite at $K_rx_0=1$ for $d>2$, and, in particular, for $d=3$. The conservation of monomers can be expressed by the equation

$$x_0+\phi_r+\phi_c=1 \tag{2.6}$$

which serves as an equation of state for the model (together with the physical requirement that x_0, ϕ_r, and ϕ_c all be non-negative).

The resulting phase diagram for $d=3$, $B=0.1$, and $K_1\to 0$ is shown in Fig. 1. The region I, where K_cx_0 and K_rx_0 are both less than unity, is the "unpolymerized" phase where the concentrations of both rings and chains decrease exponentially with length m. In the limit $K_1\to 0$, only rings are present. Region II is the Tobolsky-Eisenberg polymerized phase of long chains with small rings present. As $K_1\to 0$ the average molecular weight of the chains diverges while x_c tends to zero with ϕ_c remaining nonzero. The concentration of rings decays exponentially with length. The phase boundary between regions I and II is given by the condition that, simultaneously, $x_0+\phi_r=1$ and $K_cx_0=1$, that is, by

$$K_c[1-\phi_r(K_rK_c^{-1})]=1\ . \tag{2.7}$$

Region III consists of rings with a power-law distribution of sizes ($x_{mr}\sim m^{-(d/2+1)}$) together with a nonzero mass fraction of *infinite rings* (more strictly, rings so large that their radius of gyration is determined by the size of the container rather than by their number of monomers). No chains are present in the limit $K_1\to 0$ and only a small concentration of chains with x_{mc} decaying exponentially with m are present when K_1 is nonzero but small. It is bounded by the line $K_r=K_p^c$ for $K_c<K_p^c$ and by the line $K_r=K_c$ for $K_c>K_p^c$ where $K_p^c=(1-\phi_r^c)^{-1}$ is given by

$$K_p^c=\{1-B[\zeta(d/2)-1]\}^{-1}\ . \tag{2.8}$$

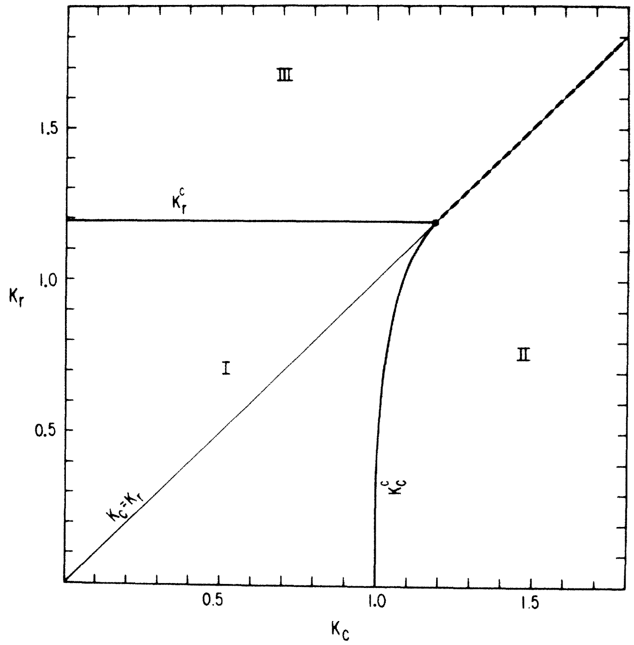

FIG. 1. Phase diagram for chemical equilibrium theory of chains and rings for $d=3$, $B=0.1$, and $K_1=0$.

The first of the lines corresponds to the condition $K_r x_0 = 1$.

The presence of the infinite rings cannot be deduced from Eqs. (2.1), but requires a careful consideration of the thermodynamic limit. In a finite container, say a cube of edge length L, the formula for x_{mr} must be modified to read

$$\begin{aligned} x_{mr} &= B m^{-(d/2+1)} (K_r x_0)^m \quad (2 \lesssim m \lesssim m^*) \\ &= B' \left[\frac{a}{L} \right]^d m^{-1} (K_r x_0 e^{-c(a/L)^2})^m \quad (m \gtrsim m^*) , \end{aligned} \tag{2.9}$$

where $m^* \sim (L/2)^2$ and a is a microscopic length of the order of the size of radius of gyration of a monomer. This may be understood as follows. The factor $m^{-d/2}$ in Eq. (2.1) is proportional to R^{-d} where R is the radius of gyration of a random walk of m monomers. For R much less than the diameter of the container, R^{+d} is the volume within which both ends of the walk are likely to be found and R^{-d} is proportional to the probability that they will be close enough to form a ring. However, when $R \gtrsim L$, this probability is no longer governed by R^{-d} but by L^{-d}, the reciprocal of the volume of the container in which they must lie. In addition to this effect there is a small entropic effect resulting in a reduction of the propagation constant K_r by the factor $\exp[-c(a/L)^2]$. This result was first obtained by Cassasa and co-workers[54] and has been obtained by a scaling argument by de Gennes.[55] We rederive it in the context of a lattice random-walk model in Appendix A. Strictly, it is valid only for $m^{1/2} a \gtrsim L$, but the further corrections for $m^{1/2} a \gg L$ do not affect the conclusion of this analysis.

Using Eq. (2.9) we obtain for ϕ_r

$$\begin{aligned} \phi_r &\approx B \sum_{m=2}^{m^*} m^{-d/2} (K_r x_0)^m \\ &\quad + B' \left[\frac{a}{L} \right]^d \sum_{m=m^*}^{\infty} (K_r x_0 e^{-c(a/L)^2})^m \\ &\approx B \sum_{m=2}^{m^*} m^{-d/2} (K_r x_0)^m \\ &\quad + \frac{B' \left[\frac{a}{L} \right]^d (K_r x_0 e^{-c(a/L)^2})^{m^*}}{(1 - K_r x_0 e^{-c(a/L)^2})} . \end{aligned} \tag{2.10}$$

For $K_r \leq K_p^c$ and $K_1 \to 0$, the second term vanishes as $L \to \infty$ and the first becomes identical to ϕ_r in Eq. (2.1). For $K_c < K_r$ and $K_r > K_p^c$, the product $K_r x_0$ must be very close to unity. Let ϕ_∞ be defined by $\phi_{r,\mathrm{tot}} = 1 - K_r^{-1} \equiv \phi_r^c + \phi_\infty$. Choose x_0 such that $K_r x_0$ is given by

$$\begin{aligned} K_r x_0 &= e^{c(a/L)^2} \left[1 - B' \left[\frac{a}{L} \right]^d \Big/ \phi_\infty \right] \\ &= 1 + c \left[\frac{a}{L} \right]^2 - B' \left[\frac{a}{L} \right]^d \Big/ \phi_\infty + O((a/L)^4) . \end{aligned} \tag{2.11}$$

Then, for very large L, the first term in (2.10) approaches ϕ_r^c while the second approaches ϕ_∞. Thus, for $K_r > K_p^c$, a fraction $\phi_\infty = 1 - \phi_r^c - K_r^{-1}$ of the monomers are incorporated in rings with $m \gtrsim m^* \sim (L/a)^2$. These "infinite" rings (in the thermodynamic limit) play the role of *a condensate* analogous to the condensate in an ideal Bose gas. Indeed, as we show in Appendix A, there is a precise mathematical analogy between the ring condensate and the condensate of the ideal Bose gas.

Despite the nonzero fraction of monomers in infinite rings the concentration x_∞ of these rings is zero in the thermodynamic limit. The total number of such rings grows only as the logarithm of the size of the system. To see this we compute the sum [using Eq. (2.9)]

$$\begin{aligned} x_\infty &\sim B' \left[\frac{a}{L} \right]^d \ln(1 - K_r x_0 e^{-c(a/L)^2}) \\ &\sim B' \left[\frac{a}{L} \right]^d \ln \left[\phi_\infty / B' \left[\frac{a}{L} \right]^d \right] . \end{aligned} \tag{2.12}$$

The total number of infinite rings is thus

$$\begin{aligned} N_\infty &\sim \left[\frac{L}{a} \right]^d x_\infty \\ &\sim \ln \left[\left[\frac{L}{a} \right]^d \right] . \end{aligned} \tag{2.13}$$

The dashed line $K_c = K_r > K_p^c$, separating regions II and III, is a first order transition line across which ϕ_c and ϕ_∞ change discontinuously but ϕ_{tot} and ϕ_r are continuous.

For $K_c > K_r$ the mass fraction of infinite rings is zero in the thermodynamic limit and the limit $K_1 \to 0$ while that of chains is nonzero, whereas for $K_c < K_r$ the opposite is true. For $K_c = K_r$ the relative amounts of chain and infinite rings depends upon the order of the limits $V \to \infty$ and $K_1 \to 0$. If the thermodynamic limit is taken before the limit $K_1 \to 0$ then only chains (and a power-law distribution of finite rings) exist on the line $K_r = K_c > K_p^c$. If the limits are taken in the opposite order, only finite and infinite rings exist. The behavior of ϕ_r, ϕ_c, ϕ_∞, and ϕ_{tot} with K_r for $K_c = 2$, $K_1 \to 0$, $B = 0.1$, and $d = 3$ is shown in Fig. 2.

It is of some interest to examine the crossover between dominance by $K_1 \to 0$ and $V \to \infty$. Chains suffer no change in prefactor from finite-size effects but do suffer the same entropic effect as rings. Thus for a finite box of edge length L the total fraction of polymerized material may be expressed in the form

$$\begin{aligned}\phi_{\text{tot}} = {} & B \sum_{m=2}^{m^*} m^{-d/2} (K_r x_0)^m \\ & + B' \left[\frac{a}{L} \right]^d \sum_{m=m^*}^{\infty} (K_r x_0 e^{-c(a/L)^2})^m \\ & + K_1 x_0 \sum_{m=0}^{m^*} m (K_c x_0)^m \\ & + K_1 x_0 \sum_{m=m^*}^{\infty} m (K_c x_0 e^{-c(a/L)^2})^m \, . \end{aligned} \tag{2.14}$$

Using Eq. (2.6) we may write, on the line $K_c = K_r = K_p > K_p^c$,

$$x_0 + \phi_r^c + \frac{B' \left[\dfrac{L}{a} \right]^{-d}}{1 - K_p x_0 e^{-c(a/L)^2}} + \frac{K_1 x_0}{(1 - K_p x_0 e^{-c(a/L)^2})^2} \cong 1 \, . \tag{2.15}$$

There will be a crossover between chains and infinite rings when the last two terms in the left-hand side of (2.15) are comparable. This occurs when

$$\left[\frac{L}{a} \right]^d \sim B' (\tfrac{1}{2} K_1 x_0 \Delta\phi_{\text{tot}})^{-1/2} \, , \tag{2.16}$$

where $\Delta\phi_{\text{tot}} \equiv \phi_{\text{tot}} - \phi_r^c$. For $\Delta\phi_{\text{tot}} \sim 1$ this gives L/a of the order of 50–100 for sulfur ($K_1 \sim 10^{-12}$). If we take $a = 6$ Å this gives $L \sim 300$ Å. Thus even with K_1 as small as 10^{-12} chains dominate for vessels larger than a few hundred angstroms. Even if K_1 were as small as 10^{-24}, the container would have to be of submicrometer dimensions to force dominance by the ring condensate. Of course, for containers this small, the large surface to volume ratio will assure that surface effects will contribute important corrections. In particular, if the effective K_1 is larger near the surface this will suppress the formation of large rings. Essentially the same conclusions follow from a nonclassical analysis of this crossover in Sec. V.

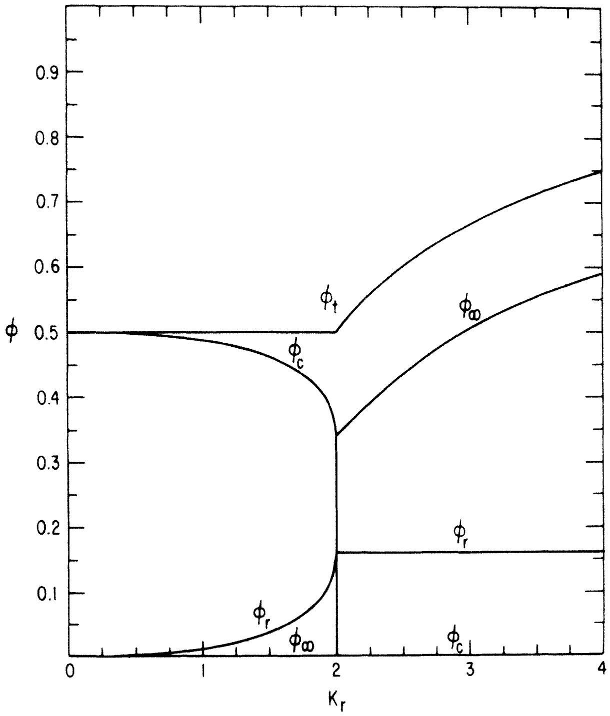

FIG. 2. Behavior of ϕ_r, ϕ_c, ϕ_∞, and ϕ_{tot} as a function of K_r for $K_c = 2$ with $K_1 = 0$, $B = 0.1$, and $d = 3$.

The behavior of ϕ_r, ϕ_c, and $\phi_{\text{tot}} = \phi_r + \phi_c$ is somewhat different along the line of physical interest, $K_r = K_c \equiv K_p$, than along a path with $K_r = \text{const}$. Along the physical line, for K_p less than a critical value, K_p^c, there are no chains in the limit $K_1 \to 0$, but both x_r and ϕ_r are nonzero. As K_p increases, $\phi_r = 1 - x_0$ increases, so x_0 decreases, but $K_p x_0$ increases. As $K_p x_0 \to 1$, the fraction of monomers in rings approaches a constant, $\phi_r^c = B[\zeta(d/2) - 1]$ where $\zeta(x)$ is the Riemann zeta function, so that $x_0^c = (K_p^c)^{-1} = 1 - \phi_r^c$. For $K_p > K_p^c$ the value of $K_p x_0$ remains at 1 (very slightly less than 1 for $K_1 \gtrsim 0$), so that ϕ_r remains constant at ϕ_r^c, while ϕ_c increases steadily with T: $\phi_c = 1 - \phi_r^c - K_p^{-1}$. Thus, ϕ_c increases linearly with $K_p - K_p^c$ just above K_p^c even in the limit $K_1 \to 0$, and all of the increase in $\phi_{\text{tot}} = \phi_r + \phi_c$ above K_p^c is due to chains. The behavior of ϕ_r, ϕ_c, and ϕ_{tot} with K_p is shown in Fig. 3 for $K_1 \to 0$, $d = 3$, and $B = 0.1$. Along the line $K_r = \text{const}$ and with $K_1 \to 0$, the fraction of polymerized material $\phi_{\text{tot}} = \phi_r$ is nonzero but constant, independent of K_c, for K_c less than a critical value K_c^c given by Eq. (2.7). For K_c greater than this value, $K_c x_0$ is equal to unity so that $\phi_{\text{tot}} = 1 - x_0$ increases linearly with K_c just above K_c^c. Since x_0 decreases, so too does ϕ_r above K_c, while ϕ_c increases. Thus, for $K_r = \text{const}$, chains grow at the expense of rings for $K_c > K_c^c$. Both ϕ_r and ϕ_c vary linearly with $K_c - K_c^c$ for $K_r < K_p^c$. When K_r is precisely K_p^c given by Eq. (2.8) the behavior of ϕ_r and ϕ_c for $K_c > K_c^c = K_p^c$ is quite different. According to Eq. (2.5), near $K_r x_0 = 1$, and for $2 < d < 4$,

$$\phi_r^c - \phi_r \sim (K_r x_0 - 1)^{d/2 - 1} \tag{2.17}$$

so that ϕ_r decreases with infinite slope just above $K_c = K_p^c$ and consequently ϕ_c must increase with infinite slope to keep $\phi_{\text{tot}}=1-x_0=1-K_c^{-1}$ increasing linearly with K_c. Similar behavior may be seen for ϕ_r and ϕ_c as functions of K_r for $K_r<K_c$ in Fig. 2.

The detailed shape of the phase boundary between regions I and II in the immediate vicinity of $K_r=K_p^c$ is of some interest. Equations (2.7) and (2.15) can be combined and rearranged to give

$$K_c-K_r \sim (K_p^c-K_c)^{2/(d-2)} \tag{2.18}$$

for $2<d<4$. This has the geometrical interpretation that the horizontal distance between a point on the phase boundary and the line of symmetry, $K_r=K_c$, in Fig. 1 vanishes as the vertical distance of this point from the critical point on the line of symmetry, $K_r=K_c=K_p^c$, raised to the power $2/(d-2)$. We will see in Sec. IV that this power should be replaced by the critical crossover exponent ϕ for quadratic anisotropy in the n-vector model in the formal mathematical limit $n \rightarrow 1$.

The phase diagram in Fig. 1 contains the confluence at the point $K_c=K_r=K_p^c$ of two "critical lines" of quite different character and a first order line. It is thus characteristic of a *bicritical phase diagram*,[56] and it is to be expected that there will be a new critical exponent describing the crossover from one type of critical behavior to the other. We argue in Secs. III and V that this exponent, ϕ, is the crossover exponent for quadratic anisotropy in the n-vector model in the limit $n \rightarrow 1$, and show in Sec. IV that, to first order in $\epsilon=4-d$, this identification is borne out by a direct calculation on a field theory of polymerization.

Although the variation of ϕ_c, ϕ_r, and ϕ_{tot} in Fig. 3 is linear with K_p near the transition to lowest order in $K_p-K_p^c$, it should not be thought that the results of this chemical equilibrium theory are "classical" or "mean field" in character. Rather, the model is described by the critical exponents of the spherical model[57] ($n \rightarrow \infty$). Thus, for example, the total fraction of polymerized material varies near K_p^c (for $K_p<K_p^c$ and $K_1=0$) as

$$\phi_r=\phi_{\text{tot}}=\phi_r^c+A(K_p-K_p^c)+C(K_p^c-K_p)^{2/(d-2)}+\cdots \ . \tag{2.19}$$

From which we can deduce that the critical exponent α for the specific heat has the value (negative for $2<d<4$)

$$\alpha=(d-4)/(d-2) \ , \tag{2.20}$$

in agreement with the spherical model.[57] Similarly the shape of the chain transition line is described by the exponent $2/(d-2)$ which is precisely the value of the crossover exponent ϕ for quadratic anisotropy in the spherical model. Using the hyperscaling relation $2-\alpha=d\nu$, we obtain $\nu=1/(d-2)$, the result for the spherical model. In Sec. V we argue that the fractal dimensionality of a long chain polymer in the presence of rings is neither $1/\nu(n=0)$ nor $1/\nu(n=1)$ but rather $\phi/\nu(n=1)$. It is interesting that the ratio ϕ/ν for the spherical model is exactly 2, independent of dimensionality, as expected for an essentially random-walk model such as this. For $d \leq 2$ the phase boundary between regions I and III recedes to $K_r=+\infty$ and there is no polymerization transition along the physical line $K_r=K_c$. (The Tobolsky-Eisenberg transition remains as K_c is increased at fixed K_r.) At $d=4$, logarithmic corrections occur in the formulas given above due to special behavior[53] of $\Phi(z,s)$ in Eq. (25) for integer s. For $d>4$ the dominant variation of ϕ_r from ϕ_r^c comes from the term with $r=1$ in (2.5) rather than from the leading term so that the exponents "stick" at their classical values. These critical and borderline dimensionalities agree with the behavior of the spherical model.

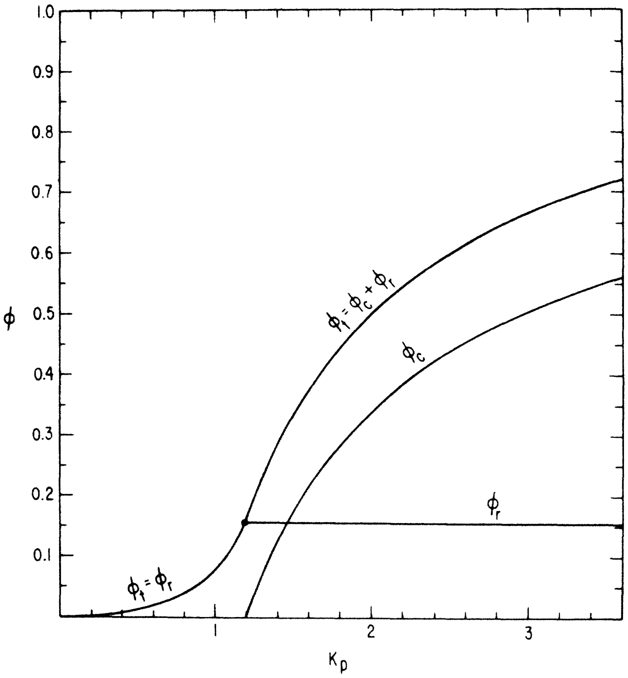

FIG. 3. Behavior of ϕ_r, ϕ_c, and ϕ_{tot} as a function of K_p with $K_r=K_c=K_p$. $K_1=0$, $B=0.1$, and $d=3$.

III. LATTICE MODEL OF CHAINS AND RINGS

In this section, we establish a connection between a lattice model of equilibrium polymerization of chains and rings and a vector model of magnetism of the same symmetry as the n-vector model of magnetism with quadratic anisotropy. Our treatment is inspired by the earlier treatment of polymerization of chains and rings by Cordery[42] and by a recent letter[52] by Nienhuis. Our treatment generalizes the work of Cordery in two important ways. First, it extends Cordery's model from strictly Ising model ($n=1$) results to general n. This allows (at least formally) the determination of the number concentration of rings as well as that of chains. Second, and more importantly, it allows the determination of the amount of polymerized material in chains and in rings separately, rather than only the total fraction of monomers in polymers as was the case for earlier treatments.

Our treatment uses the ideas of universality in two important ways. Our model of polymerization, like that of Cordery, employs a very special and somewhat artificial form for the repulsion between closely approaching polymer segments. We argue that the exponents describing the behavior of this model should not be dependent upon the details of this repulsion and should therefore be the same for our model as for a more realistic choice of interactions. Our model of magnetism, following the idea of Nienhuis, is also not the n-vector model with quadratic anisotropy, but rather a simpler model that, for small values of the anisotropy and magnetic field, has the same symmetry as the n-vector model and therefore, by universality arguments, should have the same critical exponents as the anisotropic n-vector model.

Consider first the following model of equilibrium polymerization of chains and rings. Each bond of a regular lattice contains one monomer molecule, which may be either closed (inactive) or open (active). If it is open the monomer lies along the bond with one active site capable of bonding to another active monomer at each end of the bond. We may thus think of each bond of the regular lattice as either "occupied" by an active monomer, or "empty." The partition function for the equilibrium state of this model is obtained by summing over all assignments of open or closed to each monomer (i.e., over all assignments of occupied or empty to each bond), and over all ways of connecting the open monomers to form polymers, subject to the following rules.

(1) At each vertex the maximum number of bonds is formed between active monomers. Thus, at most one active polymer end remains at any site of the lattice.

(2) At a vertex at which $2k$ or $2k-1$ active monomers meet to form k polymers, each of the $(2k-1)!! \equiv (2k-1)(2k-3)\cdots(1)$ possible ways of pairing the (distinguishable) bonds into pairs to form polymers is counted. (See, for example, Fig. 2 of Ref. 42.)

(3) Each chain polymer contributes a factor K_1 to the statistical weight of the state, each ring polymer a factor K_2, and each bond, a factor K_p'.

(4) At each vertex at which $k>2$ polymers meet, each of the $(2k-1)!!$ pairings contributes a factor $W_k<1$ to the statistical weight of that state.

This accounts for excluded-volume effects by deweighting vertices at which two or more polymers approach each other closely with the "Boltzmann factor" W_k. We will want to demand that $W_{k_1}<W_{k_2}$ whenever $k_1>k_2$, that is, that the polymers repel each other. The partition function for this model of equilibrium polymerization of chains and rings is then given by

$$Z_p=\sum{}^{(1)}\sum{}^{(2)}K_1^{N_c}K_2^{N_r}(K_p')^{N_b}\prod_{k=2}^{k_{\max}}W_k^{N_k}\ , \tag{3.1}$$

where $\sum^{(1)}$ is the sum over all assignments of occupied or empty to each bond, $\sum^{(2)}$ is the sum over all allowed ways of connecting the occupied bonds of the lattice to make polymers according to rules (1) and (2), above, and where N_c, N_r, N_b, and N_k $(k=2,3,\ldots,k_{\max})$ are, respectively, the number of chains, rings, bonds, and vertices at which k polymers meet in a given configuration. ($k_{\max}$ is the largest integer less than or equal to $q/2$ where q is the coordination number of the lattice.) Various properties of the polymer model can be obtained by differentiation of the partition function. Let

$$f_p(K_1,K_2,K_p',\{W_p\})=\left[\frac{2}{qC}\right]\ln Z_p\ , \tag{3.2}$$

where C is the number of sites on the lattice and q is the coordination number so that $\frac{1}{2}qC$ is the total number of bonds on the lattice. Then the "concentrations" of chains and rings, x_c and x_r (expressed as the number of chains or rings divided by the total number of monomers), are given by

$$x_c=\left[\frac{\partial f_p}{\partial \ln K_1}\right],\qquad x_r=\left[\frac{\partial f_p}{\partial \ln K_2}\right], \tag{3.3}$$

and the fraction of monomers incorporated in polymers, whether rings or chains, is given by

$$\phi_{\text{tot}}=\left[\frac{\partial f_p}{\partial \ln K_p'}\right]. \tag{3.4}$$

In its present form, this model does not allow the determination of the fraction of monomers incorporated in chains or in rings separately. This difficulty can be surmounted, at least formally, by allowing bonds in chains and bonds in rings to contribute differently to the statistical weight of a state. If each bond of a ring contributes a factor K_r and each bond of a chain (including a single open monomer) contributes a factor K_c, and if L_r and L_c are the total number of bonds (monomers) in rings and chains, respectively, in a given configuration, then the corresponding partition function can be expressed as

$$Z_p=\sum{}^{(1)}\sum{}^{(2)}K_1^{N_c}K_2^{N_r}K_c^{L_c}K_r^{L_r}\prod_{k=2}^{k_{\max}}W_k^{N_k}\ , \tag{3.5}$$

where the remaining notation is the same as in Eq. (3.1). In terms of the thermodynamic potential f_p, defined in analogy with (3.2), the fractions of all monomers incorporated in chains and rings are given by

$$\phi_c=\left[\frac{\partial f_p}{\partial \ln K_c}\right],\qquad \phi_r=\left[\frac{\partial f_p}{\partial \ln K_r}\right]. \tag{3.6}$$

While the formal introduction of K_c and K_r as distinct entities allows the determination of ϕ_c and ϕ_r separately, it should be emphasized that the physically relevant situation is $K_c=K_r$. While one might imagine that the statistical weight per bond might be different for rings and chains of small size, the model chosen above implies that K_r and K_c are independent of polymer size, and for very large polymers it is difficult to see how the contribution per bond could be different for rings and chains. Even long-range electronic conjugation effects which might select rings from chains must decay to zero at large enough lengths.

A similar argument suggests that the physically relevant value of K_2, the statistical weight per ring, should be unity. For a given configuration of a very large ring and a given configuration of a very large chain we would expect that the statistical weight for removing one monomer (emptying one bond) from the ring would be the same as the removing one monomer from the middle of the chain. The first process destroys one ring, creates one chain, and reduces the number of occupied bonds by one. It therefore has statistical weight (relative to the initial state) $K_1K_2^{-1}(K_p')^{-1}$. The second process decreases the number of occupied bonds by one and increases the number of chains by one. It thus has statistical weight $K_1(K_p')^{-1}$. For these processes to have equal probabilities, we must set $K_2=1$.

The argument above is appropriate for monomers that have a single distinguishable orientation or collection of configurations along a lattice bond (as is the case in sulfur), or in which the monomers have two or more distinguishable configurations but connect together randomly with propagation constant independent of configuration. If the monomers had two distinct configurations, corresponding to an arrow pointing in either direction along the bond, and if the monomers could only join head to tail, giving rise to two distinct polymers for each lattice walk, then an argument similar to the one given above leads to the conclusion that $K_2=2$ so that $n=2$ is the appropriate universality class. The case in which the two (or more) states can mix but not randomly is more complicated. It can be treated by methods similar to those that have been used recently,[58] to treat equilibrium copolymerization, and has been treated directly by universality arguments.[59]

We now turn to a model of an anisotropic magnet and show that it is related to our model of polymerization. In the limit that the anisotropy field g vanishes, the partition function of the magnet becomes identical with that in (3.1) for the polymer system. This is closely related to (although not identical with) Cordery's result. For nonzero g the magnetic model is *not* identical with the model of polymerization with $K_c \neq K_r$. However, we show that the derivative with respect to g at $g=0$ generates exactly the statistical average necessary to calculate the fraction of monomers in the chains, ϕ_c.

Consider the following model partition function for a magnet:

$$Z=\frac{\int \prod_{i=1}^{N} d\mathbf{S}_i \left[\prod_{\langle ij\rangle} e^{-V(\mathbf{S}_i,\mathbf{S}_j)} \prod_i e^{-W(\mathbf{S}_i)}\right]}{\int \prod_{i=1}^{N} d\mathbf{S}_i}\,, \tag{3.7}$$

where the integral is over all directions of the N fixed-length classical vector spins $\mathbf{S}_i$ in n dimensions, the product $\prod_{\langle ij\rangle}$ is over all nearest-neighbor pairs of spins on the lattice, and the products $\prod_i$ are over all of the N spins on the lattice.

For the n-vector model of magnetism with quadratic anisotropy, $V(S_i,S_j)$ and $W(S_i)$ would be given by

$$\begin{aligned} V(\mathbf{S}_i,\mathbf{S}_j)&=-\tilde{J}\mathbf{S}_i\cdot\mathbf{S}_j-g(\mathbf{S}_i\cdot\mathbf{S}_j-nS_i^1S_j^1)\,,\\ W(\mathbf{S}_i)&=-hS_i^1\,, \end{aligned} \tag{3.8}$$

where the dot product is given by $\mathbf{S}_i\cdot\mathbf{S}_j=\sum_{\alpha=1}^{n}S_i^\alpha S_j^\alpha$ and the vectors are of fixed length $n^{1/2}$, that is, $\sum_{\alpha=1}^{n}S_i^\alpha S_i^\alpha=n$. The first term in $V(\mathbf{S}_i,\mathbf{S}_j)$ is the usual interaction between spins in the isotropic n-vector model while the second introduces an anisotropy that selects out one component (component 1) as having either stronger or weaker coupling than the rest. According to current understanding of critical phenomena, the critical behavior of such a magnet (for integer n greater than unity) will fall into different universality classes according to whether g is negative, positive, or zero.

We will eventually be interested in the formal mathematical limit $n\rightarrow 1$. While this has no simple physical interpretation in the magnetic language, the renormalization-group expansions for critical exponents may be continued to this limit and we assume that they give the appropriate exponents for the corresponding polymer problem in that limit. We have verified this assumption to order $\epsilon=4-d$ in Sec. IV.

Equation (3.8) for $V(\mathbf{S}_i,\mathbf{S}_j)$ of the anisotropic n-vector model can be rearranged to yield

$$V(\mathbf{S}_i,\mathbf{S}_j)=-[\tilde{J}+(1-n)g]S_i^1S_j^1-(\tilde{J}+g)\sum_{\alpha=2}^{n}S_i^\alpha S_j^\alpha\,. \tag{3.9}$$

The Hamiltonian defined by Eqs. (3.7) and (3.8) can in fact be mapped to a corresponding polymerization model of chains and rings, as discussed briefly at the end of this section. Here, however, we adopt the strategy employed recently by Nienhuis[52] and consider instead the Hamiltonian defined by the following choices for $V(\mathbf{S}_i,\mathbf{S}_j)$ and $W(\mathbf{S}_i)$:

$$\begin{aligned} e^{-V(\mathbf{S}_i,\mathbf{S}_j)}&\equiv[1+\tilde{J}\mathbf{S}_i\cdot\mathbf{S}_j+g(\mathbf{S}_i\cdot\mathbf{S}_j-nS_i^1S_j^1)]\\ &=\left[1+[\tilde{J}+(1-n)g]S_i^1S_j^1+(\tilde{J}+g)\sum_{\alpha=2}^{n}S_iS_j\right],\\ e^{-W(\mathbf{S}_i)}&\equiv(1+hS_i^1)\,. \end{aligned} \tag{3.10}$$

This choice corresponds to truncating the expansion of the exponential at first order in the interactions, or, equivalently, to including additional higher-order multispin interactions in $V(\mathbf{S}_i,\mathbf{S}_j)$ and $W(\mathbf{S}_i)$. The essential observation is that for sufficiently small g and h the resulting Hamiltonian is of the same symmetry as the original, and should therefore fall into the same universality class. The Hamiltonian defined by (3.10) has the great advantage that the expansion of the partition function in powers of $\tilde{J}$, g, and h yields at most one power of $\tilde{J}$ or g from each bond and at most one power of h from each site. The resulting graphs are identical to those encountered in the hyperbolic tangent expansion for the partition function of the Ising model with the exception that each bond carries a "color" corresponding to the spin component α in the product $S_i^\alpha S_j^\alpha$ that generates it. Indeed, with $g=0$ and in the limit $n\rightarrow 1$, Eq. (3.7) with Eq. (3.10) is the partition function of the Ising model under identification

$$\tilde{J}=\tanh(J_I/kT)\,,$$
$$h=\tanh(H_I/kT)\,. \tag{3.11}$$

For general integer $n>1$, each bond of an Ising graph, G must be labeled with a color corresponding to the spin component α of the product $S_i^\alpha S_j^\alpha$ that produces it. This results in a large number of colored graphs, G_i corresponding to each Ising graph.

By symmetry, the integral $\int\prod_i d\mathbf{S}_i$ will eliminate any graphs which do not obey the following rules.

(1′) Every lattice site visited by a graph must have an even number of bonds of each color emanating from it, *with the understanding that,*

(2′) a cross (corresponding to a factor hS_i^1) plays the role of a bond of "color 1" emanating from the site, so that an odd number of (other) bonds of color 1 must emanate from a cross site. Consequently,

(3′) each graph must have an even number of sites with crosses.

The partition function for this magnetic model can thus be expressed as the sum of the statistical weights of graphs over all colorings with n colors (subject to the rules above) of all graphs in the hyperbolic-tangent expansion for the partition function of the Ising model in nonzero field.

The sum over all Ising graphs is simply the sum $\sum^{(1)}$ in (3.1) over all assignments of occupied or unoccupied to each bond of the lattice with the understanding that occupied bonds meeting at a lattice site simply meet there forming a vertex of the resulting graph. For the Ising model ($n=1$) each bond of the graph contributes a factor $\tilde{J}$ to the statistical weight and each odd vertex (vertex at which an odd number of bonds end) contributes a factor h. For the n-vector model we must sum over all colorings of the graph with n colors subject to rules (1′) and (2′) above and evaluate the statistical weights of the various kinds of resulting vertices. Each bond of color 1 in the graph contributes a factor $[\tilde{J}+(1-n)g]$ to the statistical weight of the graph, and each bond of color $\alpha\neq 1$ contributes a factor $(\tilde{J}+g)$. Each graph vertex with an odd number of bonds carriers a cross and contributes a factor h. Vertices with more than two bonds require special attention in this model. They require the calculation of spin averages other than $\langle (S^\alpha)^2\rangle_A\equiv 1$ where $\langle\ \rangle_A$ denotes the angular average over all directions in the n-dimensional spin space. We have shown earlier[25] that the angular average of a product of powers of spin components in the n-vector model can be evaluated explicitly as

$$\left\langle \prod_\alpha (S_i^{(\alpha)})^{2k_\alpha}\right\rangle_A =\frac{\Gamma(\frac{1}{2}n)}{\Gamma\left[\frac{1}{2}n+\sum k_\alpha\right]}\left[\prod_\alpha \frac{\Gamma(k_\alpha+\frac{1}{2})n^{k_\alpha}}{\Gamma(\frac{1}{2})}\right]. \tag{3.12}$$

This may be expressed in a more convenient form for the present purposes as follows. Let a vertex of interest have $2k_1$ bonds of one color, $2k_2$ bonds of a second color, etc., where $k_1\geq k_2\geq k_3\geq\cdots>0$, and where it is understood that a cross counts as a bond of color 1. Then the angular average in (3.12) at this vertex is given by

$$f_k^{k_1,k_2,\ldots}=W_k\prod_i(2k_i-1)!!\,, \tag{3.13}$$

where $k=\sum_i k_i$, and

$$W_k=\frac{\Gamma(\frac{1}{2}n)}{\Gamma(k+\frac{1}{2}n)}\,\frac{\Gamma(k+\frac{1}{2})}{\Gamma(\frac{1}{2})}\,\frac{n^k}{(2k-1)!!} \tag{3.14}$$

$$=\frac{n^{k-1}}{(n+2)(n+4)\cdots[n+2(k-1)]}\,. \tag{3.15}$$

We now observe that each colored Ising graph can be decomposed (in general, in many ways) into a configuration of colored polymers analogous to the polymer configurations described above for our polymer model, but with the additional feature that each polymer is colored with exactly one of the n colors of the n-vector model graph. If, at a given vertex, all of the k_i are unity, i.e., if no more than two bonds of any one color meet at that vertex, then the angular average is simply W_k. For such a vertex there is only one way to pair the bonds to form a polymer interpretation in which each resulting polymer consists of a single color. For a vertex with some of the k_i greater than unity there will be $\prod_i(2k_i-1)!!$ ways in which the sets of $2k_i$ bonds of the same color can be paired to form a polymer interpretation. If each of these pairings is taken to contribute a factor of W_k to the statistical weight, then the sum over all such pairings will contribute precisely the factor $f_1^{k_1,k_2,\ldots}$ in Eq. (3.13), i.e., precisely the angular average of the spin product at that vertex. In this way we may rewrite the sum over all colorings with n colors of all Ising graphs as the sum over all polymer configurations in the polymer model subject to the following observations. Every bond on the graph is unambiguously either in a ring or in a chain in any one of the interpretations. If it is in a chain, then it is connected to a cross and so is necessarily of color 1. If it is in a ring then it may be of any of the n colors, and the sum over all allowed colorings of the Ising graph will generate all n colors for every ring. We can thus write the partition function of the n-vector magnet under consideration as the sum over all assignments of occupied or empty to each bond of the lattice and over all ways of pairing bonds at vertices to form polymer configurations subject to rules (1) and (2) of the polymer model, and finally over all colorings of the rings with any of n colors and the chains with color 1 of the statistical weight of such a polymer configuration with the rules that each bond of color 1 contributes a factor $[\tilde{J}+(1-n)g]$, each bond of color $\alpha\neq 1$ contributes the factor $(\tilde{J}+g)$, each chain contributes the factor h^2, each ring of a specified color, the factor unity, and each vertex at which k polymers meet, the factor W_k in Eq. (3.15). For the case $g=0$ bonds of all colors are identical. In this case the sum over all colors for a ring contributes the factor n for each ring and the partition function for the *magnet* can be written simply as

$$Z_m=\sum{}^{(1)}\sum{}^{(2)}(h^2)^{N_c}(n)^{N_R}(\tilde{J})^{N_b}\prod_{k=1}^{k_{\max}}W_k^{N_k}\,, \tag{3.16}$$

where the notation is the same as that in Eq. (3.1) and W_k is given by Eq. (3.15). Comparing with (3.1) we see that if we make the identifications

$$\begin{aligned} &K_1 \leftrightarrow h^2 ,\\ &K_2 \leftrightarrow n ,\\ &K_p' \leftrightarrow \tilde{J} , \end{aligned} \tag{3.17}$$

and require W_k for the polymer model to be given by (3.15), then there is an exact correspondence between the two models. It is natural to define the thermodynamic potential for the spin system (magnet) as

$$f_m(h,J;n) \equiv \frac{1}{C} \ln Z_m . \tag{3.18}$$

We then have the connection

$$f_p(K_1,K_2,K_p',\{W_k\}) = \frac{2}{q} f_M(h,\tilde{J};n) . \tag{3.19}$$

Accordingly we can make the connections

$$\begin{aligned} x_c &= \frac{\partial f_p}{\partial \ln K_1} = \frac{2}{q}\frac{\partial f_m}{\partial \ln h^2} = \frac{1}{q} hm ,\\ \phi_{\text{tot}} &= \left[\frac{\partial f_p}{\partial \ln K_p'} \right] = \frac{2}{q}\frac{\partial f_m}{\partial \ln J} = \frac{2}{q}\tilde{J}e ,\\ x_r &= \left[\frac{\partial f_p}{\partial \ln K_2} \right] = \frac{2n}{q}\left[\frac{\partial f_m}{\partial n} \right] , \end{aligned} \tag{3.20}$$

where m and e are the magnetization and spin coupling energy per spin, respectively. With $g=0$ (the case of physical interest) there is no way to determine ϕ_c and ϕ_r separately. For nonzero g the magnetic model is no longer identical with the polymer model, even when $K_c \neq K_r$. However, as we now show, the derivative with respect to g in the limit $g \to 0$ generates precisely the fraction of monomers in chains. For $g \neq 0$ each ring makes two contributions of quite distinct nature, according to whether α, the color of the rings, is 1 or not. If there are L_i bonds in ring number i, then this ring makes one contribution of the factor $[\tilde{J}+(1-n)g]^{L_i}$ for $\alpha=1$ and $(n-1)$ contributions of the factor $(\tilde{J}+g)^{L_i}$ for $\alpha \neq 1$. The partition function can then be expressed in the form

$$\begin{aligned} Z_m = \sum{}^{(1)} \sum{}^{(2)} (h^2)^{N_c} [\tilde{J}+(1-n)g]^{L_c} \\ \times \prod_{k=1}^{k_{\max}} W_k^{N_k} \prod_{i=1}^{N_R} \{ [\tilde{J}+(1-n)g]^{L_i} \\ +(n-1)(\tilde{J}+g)^{L_i} \} , \end{aligned} \tag{3.21}$$

where L_c is the total number of bonds (monomers) in chains. Equation (3.21) reduces to (3.16) when $g \to 0$. We now note that

$$\lim_{g \to 0} \left[\frac{\partial}{\partial g} \{ [\tilde{J}+(1-n)g]^{L_i} + (n-1)(\tilde{J}+g)^{L_i} \} \right] = 0 . \tag{3.22}$$

Thus, we have the equality

$$\begin{aligned} \lim_{g \to 0} \left[\frac{\tilde{J}}{1-n} \right] \frac{\partial}{\partial g} (\ln Z_m) \\ = Z_m^{-1} \sum{}^{(1)} \sum{}^{(2)} L_c (h^2)^{N_c} (n)^{N_R} (\tilde{J})^{N_b} \prod_{k=1}^{k_{\max}} W_k^{N_k} , \end{aligned} \tag{3.23}$$

where $N_b = L_c + \sum_{i=1}^{N_R} L_i$ is the total number of bonds (active monomers) in the configuration. This is precisely the average number of bonds in chains. Thus, if we define $f_m(h,g,\tilde{J};n)$ in analogy with (3.18), we have

$$\phi_c = \left[\frac{2}{q} \right] \left[\frac{\tilde{J}}{1-n} \right] \left[\frac{\partial f_m}{\partial g} \right] \Bigg|_{g \to 0} . \tag{3.24}$$

From the symmetry of our magnetic model we expect it to have the same critical exponents and scaling behavior near the critical point as the n-vector model of magnetism. Consequently we expect that, near the critical point, the thermodynamic potential will have the scaling behavior

$$\begin{aligned} f_m(h,g,\tilde{J};n) \sim |\tau|^{2-\alpha} f_m^{(s)}(h/|\tau|^{\Delta}, g/|\tau|^{\phi}, \operatorname{sgn}(\tau);n) \\ + f_m^{(r)}(h,g,\tilde{J};n) , \end{aligned} \tag{3.25}$$

where $f_m^{(s)}$ carries the dominant singularities of the free energy, $f_m^{(r)}$ is a (more) regular function of h, g, and J, where $\tau = (\tilde{J}_c - \tilde{J})/\tilde{J}$, and where $\Delta = \beta\delta$ and ϕ are critical exponents. The exponent ϕ is the *crossover exponent* that describes the way in which the critical behavior crosses over from that of an $(n-m)$-vector model to that of an m-vector model as g passes through zero. We are concerned here with the (rather bizarre) limit $n=m=1$. As a consequence of this scaling form we conclude that

$$\begin{aligned} \phi_{\text{tot}} &\sim |\tau|^{1-\alpha} \phi_t^{(s)}(h/|\tau|^{\Delta}, \operatorname{sgn}(\tau)) + \phi_t^{(r)}(h,\tilde{J}) ,\\ \phi_c &\sim |\tau|^{2-\phi-\alpha} \phi_c^{(s)}(h/|\tau|^{\Delta}, \operatorname{sgn}(\tau)) . \end{aligned} \tag{3.26}$$

We see, therefore, that the critical exponent governing the growth of the fraction of monomers in chains is different, in general, from that governing the total fraction of monomers in polymers. Moreover, since the exponent ϕ in general exceeds unity, it is to be expected that the exponent governing ϕ_c is farther below unity than that governing ϕ_{tot}, so that ϕ_c grows more rapidly than ϕ_{tot} near the critical point. If we write ϕ_c in the form $\sim \tau^{1-\alpha_c}$, then the effective exponent α_c governing chains is $\alpha_c = \alpha + \phi - 1 > \alpha$.

The correspondence developed above is valid for any value of $K_2 = n$. As we argued for the polymer model, however, the appropriate value of K_2 for polymerization of sulfur chains and rings is $K_2 = 1$. We are thus led to examine the anisotropic n-vector magnet in the limit $n \to 1$. A wide variety of estimates for α are available[34–37] and the current consensus is that $\alpha(n=1,d=3) \approx 0.12$. The value for $\phi(n \to 1)$ is much less well studied, but the ϵ expansion for ϕ has been carried out to third order.[49,50] From this work we estimate $\phi(n \to 1, d=3) \approx 1.08$. It follows that $\alpha_c \approx 0.20$, substantially larger than $\alpha(n=1)\approx 0.12$ and rather close to the value $\alpha(n\to 0)\approx 0.24$ appropriate when only chains are present. For K_p' less than its critical value $K_p^c=\tilde{J}_c$ and $K_1\to 0$ it is surely the case that $\phi_c\to 0$. However, for $K_p'>\tilde{J}_c$ we expect that ϕ_c remains positive even as $K_1\to 0$ that is, that $\phi_c^{(s)}(0,-1)>0$. The only way in which the fraction of monomers in chains can grow faster than the total fraction of monomers in polymers is that the fraction of monomers in rings decrease with the same exponent as that for chains. We are thus led to conclude that, to leading order

$$\begin{aligned}&\phi_{\text{tot}}\sim\phi_r\sim\phi_r^c-A\,|\tau|^{1-\alpha}\quad(K_p<\tilde{J}_c)\,,\\&\phi_r\sim\phi_r^c-B\,|\tau|^{2-\phi-\alpha}+A'|\tau|^{1-\alpha}\quad(K_p>\tilde{J}_c)\,.\end{aligned}\tag{3.27}$$

The choice in Eq. (3.15) for the statistical deweighting factor W_k associated with the close approach to two or more polymers may seen rather arbitrary and artificial, and so is perhaps worth some further attention. One would expect on rather general grounds that such a factor should have the Arrhenius form

$$W_k\sim\exp[(T\,\Delta S_k-\Delta H_k)/RT]<1\tag{3.28}$$

with $\Delta H_k>0$ and $\Delta S_k<0$ corresponding to an unfavorable energy associated with such a site and, in addition perhaps, an unfavorable entropy associated with states unavailable at any energy. The form in (3.15) corresponds to $\Delta H_k=0$; that is, to a purely entropic effect. While this is surely unrealistic, it does at least reproduce the physically natural expectations that $W_k<1$ and that $W_{k_2}<W_{k_1}$ if $k_2>k_1$, i.e., that a vertex becomes progressively less likely as more polymers pass in close proximity. Inspection of (3.15) verifies that W_k does fall off rapidly as k increases for n near unity. As noted at the beginning of the section, we anticipate that the detailed form of W_k should not affect the gross features of the critical behavior such as critical exponents provided it retains the essential features of an excluded volume or unfavorable interaction between polymers. In fact, by considering non-fixed-length spins we may alter the form of W_k. As a result, the factor n^k in W_k, which is the average of $(\mathbf{S}\cdot\mathbf{S})^k$ for fixed-length spins of length $\sqrt{n}$ may be replaced by the $2k$th moment of any non-negative normalized probability density defined on $(0,\infty)$.

It is interesting to note that the relationship expressed in (3.13) between the angular average in (3.12) and the number of ways of pairing the bonds of the same color required for the polymer model is not an accident but rather a fundamental consequence of the O(n) symmetry of the magnetic model. This may be seen as follows. The average in Eq. (3.12), which may be written in the form $\langle\prod_{j=1}^{2k}S^{(\alpha_j)}\rangle$, may be regarded as the limit of the average (over $\mathbf{S}$) of a product of dot products of $\mathbf{S}$ with $2k$ distinct and independently variable vectors $\mathbf{V}_j$ $(j=1,2,\ldots,2k)$ in Euclidean n-space E_n. Such an average is a function of the $2k$ vectors $\mathbf{V}_j$ and is an (even) invariant of the operations of O(n), that is, of all rotations and reflections of all of the $\mathbf{V}_j$ about the origin in E_n. As such, it can be expressed[60] in terms of the n^2 possible dot products among the $\mathbf{V}_j$. Because it is linear (and homogeneous) in each of the $\mathbf{V}_j$ and independent of a permutation of the labels j on the V_j, the most general possible expression is a single constant multiplying the sum, over all distinct ways of pairing the subscripts $j=1,2,\ldots,2k$, of the product of k dot products between the $\mathbf{V}_j$ such that each vector $\mathbf{V}_j$ enters exactly once in each product. If the V_j are now allowed to approach the basis vectors in E_n, the average becomes identical with that in (3.12) in the form given above, while the dot products $(\mathbf{V}_i\cdot\mathbf{V}_j)$ approach Kronecker delta functions of the basis vector indices: unity if $\mathbf{V}_i$ and $\mathbf{V}_j$ approach the same basis vector, zero otherwise. As a consequence, the average in (3.12) may be expressed in the form

$$\left\langle\prod_{j=1}^{2k}S^{(\alpha_j)}\right\rangle=W_k\sum{}^{P}\prod_{l=1}^{k}\delta_{\beta(l),\gamma(l)}\,,\tag{3.29}$$

where the sum $\sum^P$ is over all distinct pairings of the indices $1,2,\ldots,2k$, into k pairs where $\beta(l),\gamma(l)$ are the lth pair $\alpha_i\alpha_j$ in a given pairing, and where $\delta_{\beta,\gamma}$ is the Kronecker delta function, unity if $\beta=\gamma$ and zero otherwise. The constant W_k depends upon n and k, but not on the individual k_j. Its value is not a consequence of symmetry arguments. From the properties of the delta functions we see that the sum $\sum^P$ is precisely the number of ways to pair like indices, and thus readily identify each polymer interpretation as corresponding to one term in the sum.

As noted at the beginning of this section, it is possible to use the true n-vector Hamiltonian in Eq. (3.8) rather than the caricature employed in (3.10). The result is that in the corresponding polymer model any number of active monomers can reside at each vertex and any number of chemical bonds joining them can reside on each lattice bond. The spin average at the lattice site leads to a statistical weight factor that deweights sites increasingly more severely the larger the number of active monomers that reside there, thus mimicking the excluded volume between polymers. This is essentially the mapping proposed by Helfrich and Müller.[43] It can be generalized to include quadratic anisotropy and thereby determine the critical behavior of ϕ_c and ϕ_r separately. The results for critical exponents are, of course, identical with those obtained above.

IV. DIRECT RENORMALIZATION GROUP ON THE POLYMER SYSTEM

It is well established[24,41,42] that chemical equilibrium theories like that presented in Sec. II are quantitatively incorrect in low-dimensional systems close to the polymerization transition. In particular, in fewer than four dimensions and on distance scales short compared to the correlation length there is a high probability that successive encounters of any specific long polymer are with the same (other) long polymer or itself. Thus, the fluctuations in the polymerized density have important correlations on these length scales and must be dealt with within a non-mean-field calculation. Such a calculation is discussed in this section. This renormalization-group calculation applied directly to the polymer system is essentially identical to the method of Wegner and Houghton[61] which has been applied to magnetic systems. In this section results are derived within the polymer context. The meaning, physical origin, and difference between the exponents may then be discussed.

The behavior of complex molecular systems in general and equilibrium polymerization in particular can be treated perturbatively within a Ursell-Mayer expansion.[62–65] Such a treatment for freely jointed polymers, and its equivalence to a magnetic system at the level of perturbation theory, is discussed in detail in Appendix B. In this section, we will use perturbation theory on a much simplified model and some approximations which give a good description of the long-range universal behavior (e.g., exponents and scaling functions) in "close to four dimensions."

In order to perform such a Ursell-Mayer expansion we must specify the monomer-monomer interaction potential $V(x)$ and the statistical weights for polymer configurations in the absence of interactions. We are focusing on systems in which the monomer-monomer interactions are short ranged and will, in particular, assume that the Mayer f function $f(x)=\exp[-V(x)/k_BT]-1$ may be approximated by a delta function

$$f(x)\sim -uK_p^{-2}\delta(\mathbf{x}) , \tag{4.1}$$

where

$$u=-K_p^2\int d\mathbf{x}\, f(\mathbf{x}) .$$

The importance of this approximation will be discussed below.

In an equilibrium polymerization system of this nature we expect that the statistical weight of a polymer chain will be proportional to K_1, the statistical weight associated with the ends of the polymer, and to a constant, K_p, raised to the number of monomers in the polymer. In addition, we will treat only the case in which the polymers are flexible, i.e., the case in which the noninteracting probability density for the separation of two monomers on a chain separated by a fixed (large) number of monomers is simply that for a random walk with a number of steps proportional to the number of intervening monomers. For the Ursell-Mayer expansion we must specify only the statistical weight for a polymer of arbitrary length which has n monomers at specified positions $\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_n$ along the chain, *with an arbitrary number of intervening monomers and an arbitrary number of monomers before (after) the first (last) monomer on the chain with specified position.* We work within a model in which this weight is given by

$$\mathscr{W}_n^c(\{x_1\})=\begin{cases} K_1K_pr^{-2}, \quad n=1 & (4.2\text{a}) \\ 2K_1K_p^nr^{-2}\displaystyle\prod_{i=1}^{n-1}G(\,|\mathbf{x}_i-\mathbf{x}_{i+1}|\,), \quad n>1 & (4.2\text{b}) \end{cases}$$

where $G(\,|\mathbf{x}-\mathbf{x}'|\,)$ is the probability density that a polymer have a monomer at $\mathbf{x}'$ along *one* of the two branches of the polymer given that it has a monomer at $\mathbf{x}$.

These formulas are typical of random walks[39,40] and *are derived for a particular model in Appendix B.* If we identify r with $1-K_p$, then the weight for a chain with a single identified monomer becomes equivalent to the Tobolsky-Eisenberg formula for the density of polymerized material derived in Sec. II when the extent of reaction is negligible. The fact that when the positions of additional monomers are specified the weight is simply multiplied by a factor dependent only on the relative positions of subsequent specified monomers is associated with the exponential distribution of chain lengths, in particular with the fact that the probability that the chain ends after any particular monomer is independent of the number of monomers which precede that monomer. The factor of 2 difference between Eqs. (4.2a) and (4.2b) is a statistical factor associated with the fact that in the first case the ends of the polymers are indistinguishable, in the second they are distinguishable, e.g., one is attached to the monomer at $\mathbf{x}_1$, the other to the monomer at $\mathbf{x}_n$.

We will model G, the probability density at a polymer have a monomer at $\mathbf{x}'$ on one of the two branches of the polymer given that it has one at $\mathbf{x}$, by

$$G(\,|\mathbf{x}-\mathbf{x}'|\,)=\int_{|k|<\Lambda}\frac{d\mathbf{k}}{(2\pi)^d}e^{i\mathbf{k}\cdot(\mathbf{x}-\mathbf{x}')}\frac{1}{(ck^2+r)} . \tag{4.3}$$

This form for G is also typical of random walks with this weighting,[39,40] e.g., we expect that the probability density of separation for two monomers on a polymer separated by a large number, n, of other monomers should be Gaussian with a variance proportional to n,

$$P(n,\mathbf{x})\sim(4\pi n\tilde{c})^{-d/2}\exp(-|\mathbf{x}|^2/4n\tilde{c}) . \tag{4.4}$$

Expressing the probability as a Fourier transform and summing over n with weighting K_p^{n-1} we readily find

$$\bar{G}(x)=\int\frac{d^dk}{(2\pi)^d}e^{i\mathbf{k}\cdot\mathbf{x}}\frac{1}{e^{\tilde{c}k^2}-K_p} \tag{4.5}$$

which differs from the formula given for $G(x)$ with $r=1-K_p$, $c=\tilde{c}$ only for large wave vectors k. As we do not expect the behavior near the transition to depend on the short-distance behavior (which in any case is not correctly given by the analysis above) the use of the model $G(x)$ is justified. We will choose the cutoff so that $c\Lambda^2=1$, i.e., so that the cell size Λ^{-1} is the mean square displacement of a polymer per monomer.

We must also specify the statistical weight for ring polymers with n monomers along the ring at positions $\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_n$, again with arbitrary numbers of intervening monomers. We will take this weight to be

$$\mathscr{W}_n^r(\{x\})=\begin{cases} \tfrac{1}{2}K_pG(\mathbf{x}=0), \quad n=1 & (4.6\text{a}) \\ \tfrac{1}{2}K_p^2G(\,|\mathbf{x}_1-\mathbf{x}_2|\,)^2, \quad n=2 & (4.6\text{b}) \\ K_p^nG(\mathbf{x}_n-\mathbf{x}_1)\displaystyle\prod_{i=1}^{n-1}G(\mathbf{x}_i-\mathbf{x}_{i+1}), \quad n>2 . & (4.6\text{c}) \end{cases}$$

Equation (4.6a) assumes a particular artificial statistical weight for a ring polymer consisting of a single monomer. This is convenient for the renormalization-group calculation described below and should not affect the description of the transition. The condition that breaking a bond in a large ring changes the free energy by the same amount as breaking a bond in a long chain implies that if a ring is broken between two monomers with specified (large) separation $\mathbf{x}$ and only the polymer segments between these monomers are allowed to relax, moving and adding monomers, the statistical weight must be divided by the same factor, $G(\mathbf{x})r^2/K_1$, as if a chain with two monomers with the same separation is broken and allowed to relax in the same way. The statistical weight above satisfies this property independently of the separation $\mathbf{x}$.

Given these statistical weights we may give the graphical rules for calculating the expectation value of many quantities. (A detailed treatment for a more realistic model is given in Appendix B.) In particular we draw graphs consisting of polymers on which monomers are known to have certain positions. Each such monomer must either be a monomer which interacts with other monomers or a monomer which has been distinguished as associated with the expectation value we are calculating, e.g., graphs for the polymerized monomer density have a single distinguished monomer at the origin, graphs for the density of monomers in chains have a single distinguished monomer on a chain at the origin, etc. As an example, these graphs for the density of monomers on chains are shown to low order in u in Fig. 4. The value of the graph is the integral over the positions of the monomers of the product of statistical weights of these polymers times the product over pairs of interacting monomers of the Mayer f function of their separation, divided by the symmetry factor of the graph (the number of ways that interacting monomers can be exchanged without changing the topology of the graph). The expectation value of the quantity is then the sum of the values of all such graphs.

Among the allowable graphs are ones in which monomers interact with more than one other monomer and graphs in which distinguished monomers interact with other monomers. We will neglect such graphs. This is justified if the perturbation parameter u is small and the polymers are long so that interactions of any specific monomer on a polymer are dominated by interactions of the other monomers on the same polymer. In principle the interactions of polymerized monomers with monomers near the ends of chain polymers differ from those with other polymerized monomers. We will assume these differences are negligible. It is unlikely that either of these assumptions or the formulas for f, G, and $\mathscr{W}$ are strictly correct for systems of physical interest. However, the approximation entailed in the use of these assumptions does not affect the universal long-length scale quantities discussed in this section.

The Ursell-Mayer expansion, order by order in the interaction strength u, diverges when $r=1-K_p$ is small or negative. Formally this is evident from the divergence of $G(|x-x'|)$ in (4.3). The physical reason for this divergence may be distinguished in two distinct regions. When r is negative and K_1 is sufficiently small the expansion does not give an adequate description of the polymerized phase on long-length scales, where each polymer interacts with many other polymers. In addition, for r and K_1 both sufficiently small there is a critical regime in which the expansion diverges because it does not adequately describe the conformation of a long piece of polymer between interactions with other polymers.

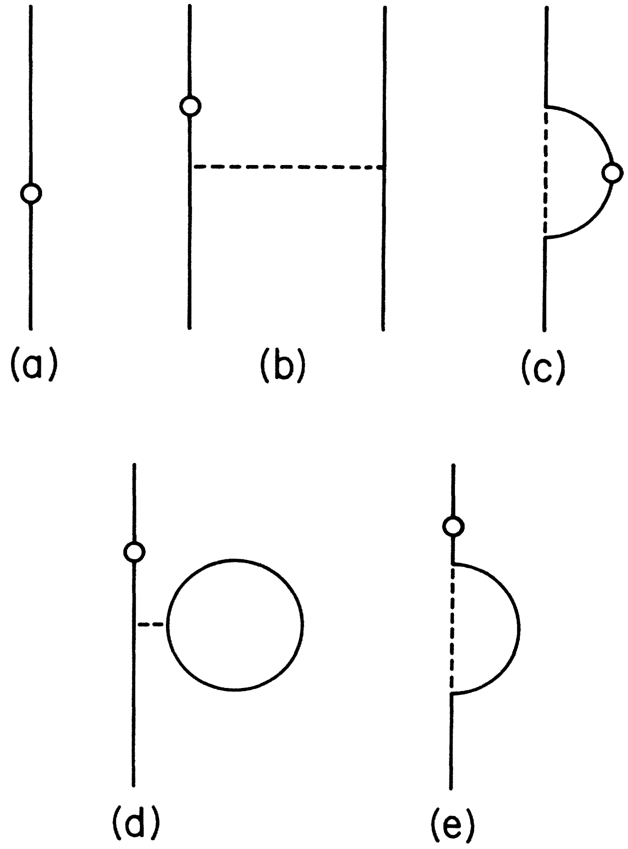

FIG. 4. Connected graphs for the density of polymerized monomers on chains to first order in the interaction u. Solid lines symbolize pieces of polymer, the open circle symbolizes the distinguished monomer on a chain polymer, and dotted lines symbolize the monomer-monomer interaction. The values of these graphs are (a) $(K_1K_pr^{-2})$, (b) $-2uK_1^2K_pr^{-5}$, (c) $-uK_1K_pr^{-2}\int dx[G(\mathbf{x})]^2$, (d) $-uK_1K_pr^{-3}G(\mathbf{x}=\mathbf{0})$, (e) $-2uK_1K_pr^{-3}G(\mathbf{x}=\mathbf{0})$.

For r sufficiently negative and K_1 sufficiently small we expect a polymerized phase in which the density of polymerized monomers is large. In order to obtain a convergent perturbation expansion in this regime we must take two effects into account. First, adding a monomer to a polymer is made less probable by its interactions with the remaining polymerized monomers. Second, the increased density of monomers on the same polymer in the vicinity of a specified monomer on a polymer is partially compensated by a decreased probability of monomers on other polymers in that vicinity. Both these effects can be treated by summing to all orders particular sets of graphs. The second effect has been treated in the literature[63] and will not be considered further in this paper. We now give a simple treatment of the first before turning to the critical region. If we assume the polymerized monomers are distributed randomly with density ϕ_{tot}, interactions with this background density will decrease the statistical weight associated with adding a monomer to a polymer by $u\phi_{\text{tot}}/K_p$ (given our assumption that a polymerized monomer interacts with only one other monomer). Thus we must replace $r=1-K_p$ in the formula for G by

$$\begin{aligned} r_{\mathrm{MF}} &= 1-K_p\left[1+\phi_{\mathrm{tot}}\int dr\, f(r)\right] \\ &= r+\phi_{\mathrm{tot}}u/K_p\ , \end{aligned} \tag{4.7}$$

where ϕ_{tot} can be determined self-consistently by the use of Eqs. (4.2a) and (4.6a):

$$\phi_{\mathrm{tot}}=\phi_c+\phi_r\ , \tag{4.8a}$$

$$\phi_c=K_1K_pr_{\mathrm{MF}}^{-2}\ , \tag{4.8b}$$

$$\phi_r=\frac{K_p}{2}\int\frac{d\mathbf{k}}{(2\pi)^d}\frac{1}{ck^2+r_{\mathrm{MF}}}\ , \tag{4.8c}$$

where ϕ_c and ϕ_r are the densities of polymerized monomers in chains and rings, respectively. These formulas are exactly those obtained from the summation of all diagrams in which no polymer has more than one interaction (not even an interaction mediated by other polymers) with any of the other polymers. This treatment is essentially identical to the chemical equilibrium treatment given in Sec. II. In particular, when $r<r_c=-u\phi_r^*/K_p$, where ϕ_r^* is the value of ϕ_r in (4.8c) with $r_{\mathrm{MF}}=0$, and $K_1\to0$, these equations have a solution with r_{MF} proportional to $K_1^{1/2}$ and $\phi_c>0$ given by

$$\phi_c\to(K_p\,|\,r\,|\,/u)-\phi_r^*\ . \tag{4.9}$$

In addition to these problems there is a divergence in the Ursell-Mayer expansion in four and fewer spatial dimensions when the polymers are long and the distance between successive interactions of a long polymer with different other polymers is large. This is because the contributions from graphs in which two pieces of polymer, having interacted once, interact with each other many more times before interacting with other polymers dominate the contributions from graphs in which these two pieces interact only once before meeting other polymers. The importance of this effect can be illustrated by giving a crude estimate of the ratio R of the contribution of a graph in which two pieces of polymer interact twice before meeting other polymers to that in which they interact only once. This may be estimated by

$$R\sim-u\int_{|\mathbf{x}|<L_{\max}}G(\,|\,x\,|\,)^2d\mathbf{x}\ , \tag{4.10}$$

where u is the contribution from the additional interaction, $G(\mathbf{x})^2$ gives the probability density that two pieces of polymer which interact at the origin both pass through x and, thus, can interact there, and $L_{\max}$ is the maximum distance scale on which it is reasonable to assume that the increase in the density over the mean density is given by a random-walk polymer, i.e., $L_{\max}$ is the lesser of the typical radius of gyration of the polymers and the typical distance scale on which a polymer encounters many other polymers. We readily find

$$R\sim-uc^{-2}L_{\max}^{4-d}\ . \tag{4.11}$$

Thus when $L_{\max}$ is large (if $d\le4$) there are clearly problems with this expansion.

This problem must be treated with the renormalization group (RG). Given the Ursell-Mayer expansion, a RG calculation can be performed directly on the polymer system. In particular we eliminate quickly varying fluctuations, change the length scale and replace monomers by "renormalized monomers," that is, pieces of polymer containing enough monomers so that the mean-square displacement of an effective monomer is equal to the new larger cell size. After these changes we find a similar system with a similar set of calculation rules but a different set of parameters. For sufficiently small initial values of u, K_1, and r these parameters will tend towards a fixed point. The universal behavior of the polymer system can then be calculated from the behavior near the fixed point.

In the RG calculation below it is not necessary to account for the screening effects discussed above that become important when the density of monomers in polymers is non-negligible. This is because we obtain RG equations only for fixed-point locations and exponents, which are independent of the direction of approach to the fixed point. If we wished to obtain the scaling form for the equation of state as well, the effects of screening would have to be considered in the semidilute limit ($K_1\to0$, $r\to0^-$).

We will eliminate fluctuations in the polymers with wave vectors k between $\Lambda e^{-\Delta l}$ and Λ. That is, we decompose the probability density G:

$$G(x)=G_S(x)+G_F(x)\ , \tag{4.12a}$$

$$G_S(x)=\int_{|k|<\Lambda e^{-\Delta l}}\frac{d\mathbf{k}}{(2\pi)^d}e^{i\mathbf{k}\cdot\mathbf{x}}\frac{1}{ck^2+r}\ , \tag{4.12b}$$

$$G_F(x)=\int_{\Lambda e^{-\Delta l}<|k|<\Lambda}\frac{d\mathbf{k}}{(2\pi)^d}e^{i\mathbf{k}\cdot\mathbf{x}}\frac{1}{ck^2+r}\ . \tag{4.12c}$$

Each Ursell-Mayer graph will then yield many new graphs in which some pieces of polymer have the quickly varying part of the propagator G_F and the remainder have the propagator G_S. We then integrate over portions of any graph which have quickly varying propagators. This yields a new "renormalized" graphical expansion for the polymer system as follows. Each portion of a graph with quickly varying propagators may be isolated from the rest of the graph by cutting all polymer lines with slowly varying propagators. The high-wave-vector (short-distance) propagators in polymer lines are considered part of a renormalized monomer. Polymer rings consisting entirely of high-wave-vector propagators are considered part of a "solvent" and are eliminated from the theory. As the rules for inserting graphical elements with quickly varying propagators are the same in all graphs these identifications yield a new set of graphical rules for the polymer differing from the rules discussed above in two ways. First the parameters discussed above: c, r, u, and K_1 will have different values. Second, possible polymer-polymer interactions and polymer statistical weights not in the rules above will be generated. The effect of these new interactions and weights decreases rapidly with length scale. In consequence they are not relevant to the calculation to lowest order in ϵ and will not be discussed below. Finally, we rescale the lengths by a factor $e^{\Delta l}$ and define a renormalized monomer, which, like the previous monomer, is sufficiently long so that, on average, it spans the larger spatial cell. This process is conceptually simpler when Δl is finite, however for mathematical convenience we will follow the common practice[34,61] of working in the limit $\Delta l \rightarrow 0$, yielding differential equations for the effective parameter as a function of length scale.

The graphs necessary to the calculation of the renormalized value of u, which are well known from the magnetic analogy, are shown in Fig. 5. From them we find the renormalization-group equation

$$du = \epsilon u\, dl - (2+2+\tfrac{1}{2}) \int d^d x [G_F(x)]^2 u^2 \qquad (4.13a)$$

with $G_F(x)$ given in (4.12c). In the limit $dl \rightarrow 0$ this becomes

$$\frac{du}{dl} = \epsilon u - \tfrac{9}{2} K_d c^{-2} \Lambda^{d-4} u^2 , \qquad (4.13b)$$

where $\epsilon = 4-d$ and $K_d = 2^{-d+1}\pi^{-d/2}/\Gamma(d/2)$ is $(2\pi)^{-d}$ times the area of the unit sphere in d dimensions. The first term comes from the scale change. As noninteracting polymers have Hausdorff dimension 2, a length rescaling by a factor of e^l will increase the number of monomers in a cell by a factor of e^{2l}. This simply corresponds to the fact that the number of steps in a random walk is proportional to the square of its linear dimension. Thus, ignoring interactions the probability that renormalized monomers in the same cell interact (e.g., the effective interaction between the renormalized monomers) increases by a factor of $\exp[(4-d)l]$. The second term gives the effect of the interactions described by the graphs of Fig. 5. The graph in Fig. 5(a) corresponds physically to the fact that the polymers have effectively smaller interactions simply because they repel each other and so are less likely than random to interact. The graph in Fig. 5(b) corresponds physically to the fact that polymers are less likely to interact because their self-interactions cause them to stretch, thus there is less likelihood of their intersecting. Finally, the graph in Fig. 5(c) corresponds to the decrease in the interaction between two polymers due to the shielding by rings, i.e., if a piece of polymer approaches another and, in doing so, displaces a large ring, the total interaction energy does not increase.

The graphs for the renormalization of the parameter r are shown in Fig. 6. We find

$$dr = 2r\, dl + (1+\tfrac{1}{2}) G_F(0) u , \qquad (4.14a)$$

where $G_F(x)$ is given in (4.12c). This gives

$$\frac{dr}{dl} = 2r + \frac{3}{2} \frac{K_d \Lambda^d}{c\Lambda^2 + r} u . \qquad (4.14b)$$

The first term simply corresponds to the change in the effective monomer in the absence of interactions: r is inversely proportional to the number of monomers in a noninteracting chain and the number of monomers in a noninteracting monomer scales as e^{2l}. The effect of interactions is given by the second term and corresponds to the decrease in free energy of a piece of polymer due to interactions with itself [Fig. 6(a)] as well as its interactions with rings [Fig. 6(b)].

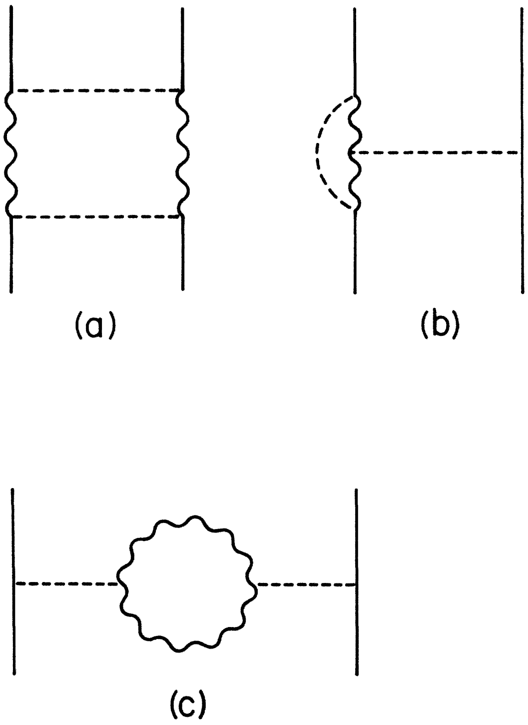

FIG. 5. Graphs for the calculation of the renormalized interaction. Slowly varying polymer propagators are symbolized by solid lines, quickly varying polymer propagators are symbolized by wavy lines, and interaction lines are symbolized by dotted lines.

The statistical weight for breaking a polymer has the renormalization-group equation

$$\frac{dK_1}{dl} = (2+d) K_1 . \qquad (4.15)$$

We have assumed that the free energy of breaking a bond between monomers is independent of environment. Thus, the only changes in K_1 come from the fact that the number of monomers in a renormalized monomer increases as e^{2l}, and the exponential of the entropy of a chain end, which when the polymer is broken can be positioned in-

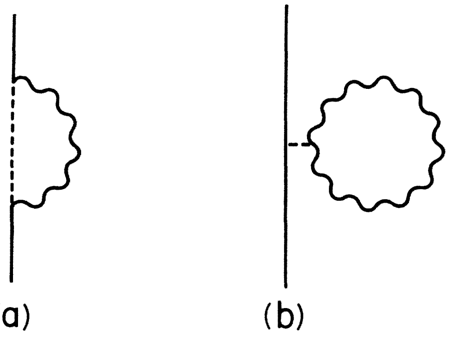

FIG. 6. Graphs of the calculation of the renormalized value of r. Symbolism is as in Fig. 5.

dependently of the other polymer, scales as the volume, e^{dl}.

To this order there are no graphs which renormalize c. Thus we do not have to adjust the rescaling equations so that c remains unity. From Eqs. (4.13) and (4.14) we then find the fixed point values to lowest order in ϵ,

$$u^c=\tfrac{2}{9}c^2\Lambda^{\epsilon}\epsilon K_d^{-1}\ , \tag{4.16a}$$

$$r^c=-\tfrac{3}{4}K_d\Lambda^{d-2}c^{-1}u_c=-\tfrac{1}{6}\Lambda^2 c\epsilon\ , \tag{4.16b}$$

$$K_1^c=0\ . \tag{4.16c}$$

We also find that

$$r(l)=r^c-(r_0-r^c)e^{l/\nu}\ , \tag{4.17a}$$

$$K_1(l)=K_1 e^{(2+d)l}\ , \tag{4.17b}$$

where we have defined

$$1/\nu=2-\epsilon/3+O(\epsilon^2)\ . \tag{4.18}$$

We may stop this renormalization-group treatment and use instead a mean-field treatment when $|r(l)-r^c|$ or K_1 is of order one; that is, when the size of the cell, Λ^{-1}, is of the order of the correlation length ξ. Then we readily see that ν is the correlation length exponent:

$$\xi\sim\Lambda_0^{-1}e^l\sim|r_0-r^c|^{-\nu}\sim|T-T_p|^{-\nu}\ , \tag{4.19}$$

where Λ_0 is the initial cutoff.

If we had employed a more general model of the polymer on short-distance scales we would obtain the same results. In particular, finite length scale interactions, finite persistence lengths for polymers, differences between monomers near to and far from the ends of polymers, etc., will all decrease rapidly in importance as we increase the length scale. Similarly, multiple interactions of monomers in polymers, interaction of a distinguished monomer with other monomers, and finite range of interactions all decrease in importance as the length scale increases. Such effects are important for calculations to higher order in ϵ, as interactions on short-distance scales result in small effective fixed-point values for these parameters.

We have calculated above the change in the effective thermodynamic parameters with a change in length scale. To calculate (for example) the density of monomers on chains we must consider the effect of the RG on graphs for this quantity. We again find (to lowest order in ϵ) that the graphical rules remain the same except that the thermodynamic parameters change and the result must be multiplied by a length-scale-dependent factor $w_c(l)$ which has the renormalization-group equation

$$dw_c=(2-d)w_c dl-\int[G_F(x)]^2 u w_c\, d^dx\ , \tag{4.20a}$$

where $G_F(x)$ is given by (4.12c). Thus,

$$\frac{dw_c}{dl}=(2-d)w_c-K_d\Lambda^{d-4}c^2uw_c\ . \tag{4.20b}$$

The first term is the effect of a change in length scale on the noninteracting polymer. When we change length scale the number of monomers in a cell through which a (noninteracting) polymer passes increases as e^{2l} because the Hausdorff dimension of this polymer is 2, while the volume increases as e^{dl} so that the density decreases as $e^{(2-d)l}$. The second term accounts for the stretching of the polymer due to its interactions with itself. It arises from graphs in which the vertex specifying that a monomer is on a chain is on a rapidly varying propagator. The relevant graph is shown in Fig. 7(a). There are additional graphs in which this vertex is on a rapidly varying propagator which yield contributions to the chain density with different graphical rules. These contributions decrease rapidly with length scale and are not important to lowest order in ϵ. From Eq. (4.20b) we find that at the fixed point ($u=u^c$)

$$w_c(l)=w_c^0 e^{l(D_h-d)}\ , \tag{4.21}$$

$$D_h=2-\tfrac{2}{9}\epsilon\ . \tag{4.22}$$

We must stop the renormalization group when the cutoff is of the order of the correlation length. In the limit $K_1\rightarrow 0$ this implies $r(l)$ is of order one and we find from Eq. (4.9) that for $r(l)$ negative the chain density of the renormalized system is a finite constant. We conclude that

$$\phi_c\sim\xi^{D_h-d}\sim|T-T_p|^{\nu(d-D_h)} \tag{4.23}$$

which is in agreement with the magnetic results of Sec. III if we use the hyperscaling formula $\nu d=2-\alpha$ and make the identification

$$D_h=\phi/\nu\ . \tag{4.24}$$

We readily verify that Eq. (4.22) is consistent with the ϵ expansion of the magnetic exponents[49] to the order to which we have calculated D_h.

It is important to remark that $D_h=\phi/\nu$ is the Hausdorff dimension of the polymer. In calculating the renormalization of the vertex we have essentially calculated the density of monomers on a long polymer in a cell provided it passes through that cell. In particular, the vertex measures the density in a cell and the sum of graphs which can be attached to it simply give the probability that the polymer pass through the cell. Equation (4.20) implies that this density scales as L^{D_h-d} where L is the length

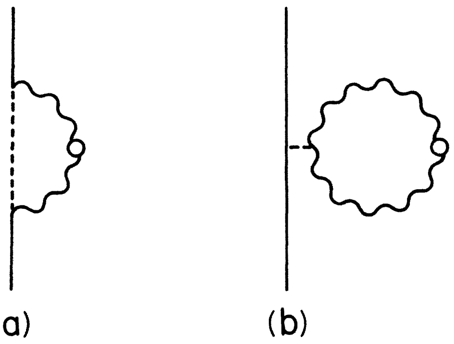

FIG. 7. Graphs for the renormalization-group calculation of the density of polymerized monomers on chains and rings. Symbolism is as in Fig. 5 except that small open circles are used to symbolize the distinguished monomer.

scale. This may be taken as a definition of the Hausdorff dimension.

It is important to emphasize that the total change from the mean of the density of monomers in a volume given that a specific long polymer passes through this volume is *not* the density of monomers on that polymer. In fact this change has a different scaling behavior. If we wanted to calculate this change we would have to include the decrease in the probability that there are small rings in the volume because a long polymer passes through. This is expressed by the graph of Fig. 7(b). We then find that the RG equation for w_{tot}, the factor by which we must multiply graphs for this density, is

$$\frac{dw_{\text{tot}}}{dl}=(2-d-\tfrac{3}{2}K_d\Lambda^{d-4}c^{-2}u)w_{\text{tot}} \tag{4.25}$$

by analysis essentially identical to that given for w_c above. We note that at the fixed point (at least to order ϵ)

$$2-d-\tfrac{3}{2}K_d u^c=1/\nu-d \text{ so } w_{\text{tot}}(l)\sim w_{\text{tot}}^0 e^{l(1/\nu-d)}.$$

In order to calculate the dependence of the total density on temperature we must take into account the fact that rings smaller than the correlation length have a density which depends on temperature. The resulting RG equation for the total density is

$$\frac{d\phi_{\text{tot}}}{dl}=\tfrac{1}{2}G_F(0)w_{\text{tot}}=\frac{\tfrac{1}{2}K_d}{c\Lambda^2+r(l)}w_{\text{tot}} \; . \tag{4.26}$$

We must integrate this equation until $e^l\Lambda\sim\xi$, do the appropriate mean-field analysis, and, finally, analyze the results. Analyses of similar RG equations (for the free energy) have been done in the past.[66] For this equation these techniques yield

$$\phi_t\sim\phi_t^{\text{reg}}(T-T_c)+\phi_t^{\text{sing}} \; , \tag{4.27}$$

where ϕ_t^{reg} is a smoothly varying, analytic function of $T-T_c$ and ϕ_t^{sing} is the singular part. This singular part has the scaling behavior of w_{tot}, that is, $|T-T_c|^{1-\alpha}f(\pm,h/|T-T_c|^{\Delta})$.

It is of some interest to note that the Hausdorff dimension of chains is slightly different if rings cannot be formed. If rings cannot be formed we would exclude the graph of Fig. 5(c), changing slightly the fixed-point value of u to be inserted in (4.20b), and thereby yielding a slightly smaller Hausdorff dimension

$$D_h(n=0)=2-\tfrac{2}{8}\epsilon+O(\epsilon^2) \; . \tag{4.28}$$

The larger Hausdorff dimension when rings can be formed is the effect of shielding by large rings. We note that if rings are not allowed we have the identity $D_h(n=0)=1/\nu(n=0)$, where $\nu(n=0)$ is the correlation length exponent for the $n=0$ magnet model, appropriate when rings are not allowed. This is because, in the polymerized phase, the fluctuations in the *total* polymerized density within a chain are simply the fluctuations in the density of that chain. This does not hold if rings can form, due to the suppression of small rings by large polymers [Fig. 7(b)].

It is also of some interest to calculate what the behavior of the system would be if the free-energy change for adding a monomer to a ring polymer were different from that for adding a monomer to a chain polymer. In this case the preceding Ursell-Mayer analysis is correct except that we must use different probability density G for rings and chains, in particular

$$G_r(x)=\int_{|k|<\Lambda}\frac{d\mathbf{k}}{(2\pi)^d}e^{i\mathbf{k}\cdot\mathbf{x}}\frac{1}{(ck^2+r_r)} \; , \tag{4.29a}$$

$$G_c(x)=\int_{|k|<\Lambda}\frac{d\mathbf{k}}{(2\pi)^d}e^{i\mathbf{k}\cdot\mathbf{x}}\frac{1}{(ck^2+r_c)} \; . \tag{4.29b}$$

As is discussed in Sec. II we expect three phases to exist in the r_r, r_c plane, an unpolymerized phase containing, in the limit $K_1\rightarrow 0$, no chain polymers and small rings, a polymerized phase containing infinite-ring polymers and a polymerized phase containing infinite-chain polymers. In order to find the location of the phase boundaries between these phases when r_r and r_c are small we must calculate their renormalized values. We will assume that the interactions between all monomers are initially the same, nevertheless, we must, in principle, distinguish three separate renormalized interactions u_{rr}, u_{rc}, and u_{cc}; those of rings with rings, rings with chains, and chains with chains. However, as long as the difference between r_r and r_c is sufficiently small all these effective interactions will be equal and have the renormalization-group equation of Eq. (4.13). The free-energy changes for adding monomers are renormalized, as before, by polymer self-interactions and by interactions with long rings (Fig. 6) yielding the renormalization-group equation

$$\frac{dr_r}{dl}=2r_r+\tfrac{3}{2}K_d u\Lambda^d\frac{1}{c\Lambda^2+r_r} \; , \tag{4.30a}$$

$$\frac{dr_c}{dl}=2r_c+K_d u\Lambda^d\left[\frac{1}{c\Lambda^2+r_c}+\frac{1}{2}\frac{1}{c\Lambda^2+r_r}\right] . \tag{4.30b}$$

From these equations we find the fixed-point values

$$u^c=\tfrac{2}{9}c^2\Lambda^{\epsilon}\epsilon K_d^{-1} \; , \tag{4.31a}$$

$$r_r^c=r_c^c=\tfrac{3}{4}K_d\Lambda^{d-2}c^{-1}u_c=-\tfrac{1}{6}\Lambda^2 d\epsilon \; . \tag{4.31b}$$

We can also find that

$$r_r-r_r^c=(r_r^0-r_r^c)e^{l/\nu} \; , \tag{4.32a}$$

$$(r_c-r_r)=(r_c^0-r_r^0)^{l\psi/\nu} \; , \tag{4.32b}$$

where ν is the previously defined exponent and $\psi=\phi$ to lowest order in ϵ.

This renormalization group must be reconsidered on a length scale l_1, where either r_r or r_c is of order one. There are then two possibilities; either mean-field theory is adequate on this length scale or there are critical fluctuations in the densities of rings or chains on length scales large compared to l_1 and these fluctuations must be treated with the renormalization group. Mean-field theory will be adequate if both r_r and r_c are of order one and positive as the polymers are then exponentially localized on the length scale l_1; this corresponds to the unpolymerized phase, i.e., we are in region I of the phase diagram of Fig. 1. Mean-field theory will also be adequate if either r_r

or r_c is negative and of order one. In this case the mean-field treatment will yield a finite condensate density of rings if $r_r < r_c$ or of chains if $r_c < r_r$. The density of this condensate is sufficiently large so that the density fluctuations decay exponentially with a length scale comparable to l_1 so that the mean-field theory is legitimate. We note that $r_r - r_c$ does not change sign under the renormalization-group transformation and thus the line $r_r^0 = r_c^0$ for $r^0 < r^c$ is a first-order transition line. Thus in this situation $r_r > r_c$ implies we are in region II of Fig. 1, $r_r < r_c$ implies we are in region III. Finally, if r_r or r_c is positive and of order one on the length scale l_1 and the other of r_r and r_c is small, it is possible to eliminate the fluctuations in one of the types of polymers by mean-field theory but a renormalization-group theory must be applied to the fluctuations in the remaining type of polymer.

Next consider the phase boundary between regions I and III in Fig. 1. When r_c is of order one and positive and r_r is small, which implies $r_r^0 < r_c^0$, we eliminate the fluctuations in chain polymers. However, this elimination is trivial as, in the limit $K_1 \to 0$, there are no chain polymers for r_c positive. Thus r_r and u are unchanged by this process. In addition the renormalization-group equations are unchanged except that u must now be interpreted as a ring-ring interaction constant. Thus $r_r^0 > r^c$ implies $r_r > r^c$ on the length scale l_1 which implies r_r will become positive and of order one on some larger length scale. If $r_r^0 < r^c$, r_r will become negative and of order one on some larger length scale. Thus the line $r_r^0 = r^c$ is the equation for the line between regions I and III in Fig. 1; the shape of the line is exactly the same as in the chemical equilibrium theory.

Finally, consider the phase boundary between regions I and II. That is, consider $r_c^0 < r_r^0$. Then on the length scale l_1 we must eliminate the fluctuations in the ring polymers and use a renormalization group appropriate to chains alone. To eliminate the rings we integrate over all wave vectors rather than just a shell of wave vectors yielding

$$r_c(l_1) = r_c(l_1) + u^c(\tfrac{1}{2}) \int_{|k| < \Lambda} \frac{d\mathbf{k}}{(2\pi)^d} \frac{1}{ck^2 + r_r(l_1)} , \tag{4.33a}$$

$$\bar{u}(l_1) = u^c - (u^c)^2(\tfrac{1}{2}) \int_{|k| < \Lambda} \frac{d\mathbf{k}}{(2\pi)^d} \frac{1}{ck^2 + r_r(l_1)} . \tag{4.33b}$$

We must then continue with a renormalization-group treatment of the chains alone. The RG equations appropriate in this case can be deduced from Eqs. 5(a), 5(b), and 6(a) to be

$$\frac{dr_c}{dl} = 2r_c + K_d u \Lambda^d / (c\Lambda^2 + r_c) , \tag{4.34a}$$

$$\frac{du}{dl} = \epsilon u - 4K_d c^{-2} \Lambda^{d-4} u^2 . \tag{4.34b}$$

From this equation we readily deduce that

$$\bar{r}_c(l_1) + \Lambda^{d-2} K_d \bar{u}(l_1)/2c = 0 \tag{4.35}$$

(for small $\bar{u}$) separates renormalization-group trajectories which flow to r_c positive and of order one and r_c negative and of order one; thus it is the equation of the critical line between the polymerized phase with infinite chains and the unpolymerized phase. As we stop the renormalization-group treatment for rings and chains when $r_r(l_1)$ is a specified constant of order one we readily find from Eqs. (4.32) and (4.34)

$$\bar{r}_c = \bar{c} + (r_c^0 - r_r^0) e^{l_1/\nu} ,$$

$$\bar{u} = \bar{c}' ,$$

$$(r_r^0 - r^c) e^{l_1/\nu} = \bar{c}'' ,$$

where $\bar{c}, \bar{c}', \bar{c}''$ are all constants. Substituting into Eq. (4.34) and recalling $r_r = 1 - K_r$, $r_c = 1 - K_c$, we find that the critical curve is of the form $(K_r^c - K_c^c)^\phi \sim |\frac{1}{2}(K_r^c + K_c^c) - K_p^c|$. Thus the chemical equilibrium theory of Sec. III gives an essentially correct phase diagram except that the spherical model exponent $2/(d-2)$ should be replaced by ϕ. Of course, the derivation given here identifies the exponent describing the shape of the phase boundary between regions I and II as equal to the crossover ϕ of the O(n) vector model for $n = 1$ only to first order in ϵ. We expect that this will hold to all orders in ϵ, but have as yet made no effort to verify this.

V. FIELD-THEORETIC ANALOGY

In Sec. IV we have applied a renormalization-group calculation directly to the polymeric system. It is known, however (Refs. 42, 45, and 48, and Appendix B), that an equilibrium polymerization system in which rings can form is analogous to an $n = 1$ magnetic model. We have previously demonstrated[48] that the chain density corresponds to a quadrupole operator in the magnetic analogy. In this section we will demonstrate that various densities and correlation functions between monomers on specific polymers correspond to the correlation functions of various different quadrupole operators in the analogous magnet. These operators all have the same scaling behavior corresponding to a single Hausdorff dimension for all the polymers. This Hausdorff dimension will be shown to be ϕ/ν in the magnetic analogy, where ϕ is the crossover dimension for the uniaxial quadratic anisotropy and ν is the correlation length exponent.

We consider an O(n) Landau-Ginsburg model with quadratic anisotropy defined by the Hamiltonian $\overline{\mathscr{H}} = \overline{\mathscr{H}}_0 + \overline{\mathscr{H}}_1$ ($\overline{\mathscr{H}} = \beta\mathscr{H}$),

$$\overline{\mathscr{H}}_0 = \int d\mathbf{x} \, \tfrac{1}{2} [\, |\nabla\sigma(x)|^2 + r\sigma^2(x) + gQ_{\alpha\beta}\sigma_\alpha(x)\sigma_\beta(x)] , \tag{5.1a}$$

$$\overline{\mathscr{H}}_1 = \tfrac{1}{8} \int d\mathbf{x} \int d\mathbf{x}' \, \sigma^2(x) u(x - x') \sigma^2(x') - h \int d\mathbf{x} \, \sigma^{(1)}(x) , \tag{5.1b}$$

where

$$\sigma^2 = \sum_\alpha |\sigma^{(\alpha)}(x)|^2 \quad \text{and} \quad \sum_\alpha Q_{\alpha\alpha} = 0 . \tag{5.1c}$$

Here, and throughout this section, we use the convention that repeated indefinite indices are summed over. This Hamiltonian differs from that used in previous work[48] by factors which do not affect universal results. They do, however, give a more consistent interpretation of the polymeric system; details are given in Appendix B.

The identification of this field theory with the Ursell-Mayer expansion of the polymeric system, as is detailed in Appendix B, is made by expanding the field theory in the perturbation $\mathscr{H}_1$. We can readily verify, provided we assume that the identified monomers do not interact with other monomers, that the chain density is proportional to the expectation value of a quadrupole operator, in particular,

$$\phi_c = \langle \tfrac{1}{2} Q_{\alpha\beta}\sigma^{(\alpha)}\sigma^{(\beta)} \rangle \ , \tag{5.2}$$

where $Q_{11}=1$ and $\sum_\alpha Q_{\alpha\alpha}=0$. As argued in Ref. 48 and in Sec. III above, the expected scaling form for ϕ_c is then

$$\phi_c \sim |T-T_p|^{2-\alpha-\phi} f_c(\mathrm{sgn}(T-T_p), h/|T-T_p|^{\Delta}) \ , \tag{5.3}$$

where f_c is a universal function and $\sim$ means asymptotically as the critical temperature is approached, i.e., when the Hamiltonian has its fixed-point value.

In fact, we can easily calculate this function to lowest (i.e., zeroth) order in $\epsilon = 4-d$, where d is the dimensionality of space, in order to verify that ϕ_c is in fact nonzero. Two factors are calculated in order to calculate a quantity in the presence of long-range fluctuations: (1) a multiplicative "renormalization factor" which arises from the effects of the short-wavelength fluctuations and (2) the results of a calculation on length scales comparable to the correlation length. Following the treatment of Schafer and Horner[67] we write

$$\langle Q_{\alpha\beta}\sigma_\alpha(\mathbf{x})\sigma_\beta(\mathbf{x})\rangle = Z_Q^{-1}\langle Q_{\alpha\beta}\bar{\sigma}(\mathbf{x})\bar{\sigma}(\mathbf{x})\rangle \ , \tag{5.4}$$

where σ is the unrenormalized spin density, $\bar{\sigma}$ is the renormalized spin density which describes the system on length scales comparable to the correlation length, and Z_Q is the renormalization factor for the quadrupole operator. We deduce from the scaling analysis, e.g., Eqs. (1.3), (3.26), (4.23), (4.24), and (5.3) above, that $Z_Q = A_Q\kappa^{\phi/\nu-2+\eta}$, where A_Q is a constant which is *not* expected to be universal, but is expected to be of order unity, and where κ is (one of the essentially equivalent definitions of) the inverse correlation length, and is given by

$$m^2 \equiv |\langle\sigma_1\rangle|^2 = (1-w^2)\kappa^{d-2+\eta}A_1/u^c \tag{5.5}$$

[cf. Ref. 67, Eq. (5.1), with appropriate changes of notation]. The parameter w is found from the equation of state, which, to lowest order in ϵ, is given by[67]

$$\begin{aligned} x &\equiv \frac{T-T_c}{|m|^{1/\beta}} = (1-w^2)^{-1/2\beta}[-1+3w^2+O(\epsilon)] \ , \\ y &\equiv \frac{h}{|m|^{\delta}} = 2w^2(1-w^2)^{(1-\delta/2)}[1+O(\epsilon)] \ , \end{aligned} \tag{5.6}$$

where the units of h, $T-T_c$, and m have been chosen so that (to lowest order in ϵ) $x=-1$ along the coexistence curve ($h=0$, $T<T_c$) and $y=1$ at $T_1=T_c$ ($x=0$). In order to deduce ϕ_c it is now necessary to calculate the right-hand side (RHS) of Eq. (5.4) to lowest order in ϵ using the fixed-point (renormalized) value of u. We readily verify that the $Q_{11}\langle\bar{\sigma}_1\rangle\langle\bar{\sigma}_1\rangle$ term dominates the fluctuation terms $(\langle\bar{\sigma}_1 - \langle\bar{\sigma}_1\rangle)^2 - \langle\bar{\sigma}_2^2\rangle$ (i.e., is of relative order ϵ^{-1}). This gives

$$\phi_c = \mathrm{const}\times(1-w^2)\kappa^{d-\phi/\nu} + O(\epsilon) \ . \tag{5.7}$$

This can be combined with the equation of state calculated by Schäfer and Horner for all w to first order in ϵ and put into the convenient parametric form of Schofield, Litster, and Ho.[68] Letting $\theta^2 = 1-w^2$ and $\tau = (T-T_c)/T_c$, one can put Eqs. (8.6)—(8.8) of Ref. 67 and Eq. (5.7) above in the form

$$\begin{aligned} m &= r^{\beta}\theta \ , \\ h &= 2r^{\beta\delta}\theta(1-\theta^2)\left[1-\tfrac{1}{2}\epsilon\left[\frac{9}{n+8}\ln 3 - \ln 2 - 1\right] + O(\epsilon^2)\right] \ , \\ \tau &= r\left\{2-3\theta^2+\epsilon(1-\theta^2)\left[1+\frac{n-1}{n+8}\left[\frac{(1-\theta^2)^{-\epsilon/2}-1}{\epsilon/2}\right]\right] \right. \\ &\qquad \left. + O(\epsilon^2)\right\} \ , \\ \phi_c &= \phi_0 r^{2-\alpha-\phi}\theta^2[1+\epsilon g(\theta)+O(\epsilon^2)] \ , \end{aligned} \tag{5.8}$$

where, again, the units of m and h have been chosen so that, to lowest order, $\tau/|m|^{1/\beta} = -1$ where $\theta^2 \to 1$ and $h/|m|^{\delta} = 1$ where $\tau = 0$, and where ϕ_0 is a numerical constant of order unity proportional to A_Q^{-1} and $g(\theta)$ is a function that we do not determine here. We anticipate that the first order (in ϵ) correction to ϕ_c will be proportional to $\epsilon/(n+8)$ and will therefore be numerically small. Brezin, Le Guillou, and Zinn-Justin[69] have obtained expressions for correlation functions of the n-vector model in unexponentiated form from which the term in ϕ_c which is first order in ϵ could in principle be calculated. For $n=1$, the case appropriate for chains and rings, the "Goldstone mode" term in τ, proportional to $(n-1)$, drops out. Equation (5.8) is valid for general n and, in particular, in the limit $n \to 0$ where it provides an equation of state for the polymerization of chains alone. To lowest order in ϵ it is very similar[70] to the parametric equation of state proposed earlier in Ref. 24.

It is of some interest to compute the light scattering from a single identified chain, or ring, i.e., the correlation function between monomers on a specified chain $[S^c(x-x', T-T_p, h)]$ or ring $[S^r(x-x', T-T_p, h)]$. This allows computation of the radius of gyration and Hausdorff dimension of such polymers. These correlation functions are given by

$$S^c(|x-x'|, T-T_p, K_1) = \tfrac{1}{4}\langle Q^c_{\alpha\beta}\sigma_\alpha(x)\sigma_\beta(x)Q^c_{\gamma\delta}\sigma_\gamma(x')\sigma_\delta(x')\rangle \ , \tag{5.9a}$$

$$S^r(|x-x'|, T-T_p, K_1) = \tfrac{1}{2}\langle Q^r_{\alpha\beta}\sigma_\alpha(x)\sigma_\beta(x)Q^r_{\gamma\delta}\sigma_\gamma(x')\sigma_\delta(x')\rangle \tag{5.9b}$$

with appropriate conditions on $Q^c_{\alpha\beta}$ and $Q^r_{\alpha\beta}$. Arguments similar to those used to discuss the chain density imply that if there are monomers at x and x', and if these monomers are on the same chain, there is a contribution proportional to $Q_{1\alpha}Q_{\alpha 1}$; if on different chains, Q^2_{11}; if on the same ring, $Q_{\alpha\beta}Q_{\beta\alpha}$; and if on different rings, $(\sum_\alpha Q_{\alpha\alpha})^2$. Thus there are four constraints on the quadrupole operators Q^c and Q^r which can be satisfied only if a distinction is made between the various magnetic components transverse to the "1" component. An example of a solution is

$$Q^c_{\alpha\beta}\sigma^{(\alpha)}\sigma^{(\beta)}=\sigma^{(1)}\sigma^{(\gamma)}+i\sigma^{(\gamma)}\sigma^{(\delta)}\ , \tag{5.10a}$$

$$Q^r_{\alpha\beta}\sigma^{(\alpha)}\sigma^{(\beta)}=\sigma^{(\gamma)}\sigma^{(\delta)}\ . \tag{5.10b}$$

$\sigma^{(\gamma)},\sigma^{(\delta)}$ are different transverse components of the magnetization, e.g., γ, $\delta\neq 1$, $\gamma\neq\delta$, and $i^2=-1$. The non-Hermitian quadrupole tensor (5.10a) cannot be made Hermitian in any way of which we are aware and is essentially a device for writing the chain-chain correlation as a difference of two magnetic correlation functions. We expect the scaling forms

$$\begin{aligned}S^c(|x|,T-T_c,h)&\\ \sim|T-T_c|^{4-2\phi-2\alpha}&\\ \times\mathscr{S}^c(\mathrm{sgn}(T-T_c),|x|\,|T-T_c|^{\nu},h\,|T-T_c|^{-\Delta}),&\end{aligned} \tag{5.11a}$$

$$\begin{aligned}S^r(|x|,T-T_c,h)&\\ \sim|T-T_c|^{4-2\phi-2\alpha}&\\ \times\mathscr{S}^r(\mathrm{sgn}(T-T_c),|x|\,|T-T_c|^{\nu},h\,|T-T_c|^{-\Delta})\ ,&\end{aligned} \tag{5.11b}$$

where $\mathscr{S}^c$ and $\mathscr{S}^r$ are universal functions. One way to obtain the power of $|T-T_c|$ in Eqs. (5.11) is to recognize that the integral of the correlation function over d-dimensional space is a generalized susceptibility and is therefore a second derivative of the free energy with respect to the conjugate field g. As such it will have an exponent of $|T-T_c|$ equal to $2-\alpha-2\phi$. The integral over space introduces d factors of the correlation length. Using the scaling law $d\nu=2-\alpha$ the powers in Eqs. (5.11) follow for the correlation function itself. Alternatively, one may deduce that the quadrupole operator itself scales as length to the exponent $(\phi/\nu-d)$ from the behavior of ϕ_c and ϕ_r near T_p and then deduce the behavior of the product of two quadrupole operators from this.

We will not give a detailed derivation for the form of the correlation functions here. However, we will discuss the expected form of the scaling function $\mathscr{S}^c$ in certain limits. When the separation between the two points in the correlation function is small compared to the correlation length, i.e., when $x\,|T-T_c|^{\nu}$, and $xh^{\nu/\Delta}$ are small, we may deduce the $|T-T_c|$ and h dependence of the function $\mathscr{S}^c$ by remarking that on distance scales large compared to x the operator

$$Q^c_{\alpha\beta}\sigma_\alpha(x')\sigma_\beta(x')Q^c_{\gamma\delta}\sigma_\gamma(x+x')\sigma_\delta(x+x')$$

is "local." Thus its behavior is determined by its symmetry. It is easy to verify that, in fact, the most divergent operator in this combination has the same symmetry as the chain density operator. Thus, we see that

$$\mathscr{S}^c(\pm 1,X,H)\sim Cf^c(\pm 1,H)X^{(\phi/\nu-d)} \tag{5.12}$$

for $X\ll 1$, $XH^{\nu/\Delta}\ll 1$, where $X=x\,|T-T_c|^{\nu}$, $H=h\,|T-T_c|^{-\Delta}$, where C is a constant, f^c is the universal chain density function given above and the power-law dependence on X and the power for X has been deduced from the required scaling form for $\mathscr{S}^c$. Equations (5.12) and (5.11a) can be combined to give

$$S^c(|X|,T-T_c,h)\sim\phi_c(T,h)X^{\phi/\nu-d}\ . \tag{5.13}$$

This formula has a simple interpretation in the polymer analogy; ϕ_c is the probability that a chain polymer has a monomer at position x' and $X^{\phi/\nu-d}$ is proportional to the probability that another monomer on the same chain be some (large) distance x away. The scaling form for the density-density correlation function is exactly what is expected for a fractal with Hausdorff dimension ϕ/ν. This implies that the Hausdorff dimension of chain polymers on distances small compared to the correlation length can be identified with this magnetic exponent, as was suggested by the calculation to low order in ϵ in Sec. IV. It is physically evident that a portion of a long ring will be locally indistinguishable from a long chain. Thus we conclude that a ring also has Hausdorff dimension ϕ/ν on length scales short compared both to the size of the ring and the correlation length.

Another limit in which the scaling behavior of $\mathscr{S}^c$ is easy to deduce is the limit of large separation and small field, i.e., $x\,|T-T_c|^{\nu}\gg 1$ and $h\,|T-T_c|^{-\Delta}\ll 1$. On these length scales in a magnet we expect the long-range fluctuations associated with the $n-1$ Goldstone modes to determine the long-distance behavior of the correlation functions. Thus it is the symmetry of the operator $Q^c_{\alpha\beta}\sigma_\alpha\sigma_\beta$ with respect to the $\mathrm{O}(n-1)$ group excluding the field direction which is of interest. We readily verify that this symmetry is that of a vector plus a quadrupole operator. The vector is dominant in the correlation functions so we deduce

$$\mathscr{S}^c\sim\int d^dk\,e^{i\mathbf{k}\cdot\mathbf{x}}k^{-2}\sim x^{2-d}\ , \tag{5.14}$$

where k^{-2} is the susceptibility for a Goldstone mode with wave vector k. For the scaling powers to be correct we find

$$S^c\sim C'\phi^c\xi^{\phi/\nu-d}X^{2-d}\ , \tag{5.15}$$

where C' is a constant. This has a simple interpretation within the "blob" model[55] of polymers. In this model polymers which have radii of gyration large compared to the correlation length are considered to be formed of connected "blobs" each having a size roughly the correlation length. Inside the blobs the polymers are expanded and excluded-volume effects are important. The connected blobs themselves form a polymer melt, the blobs on large enough length scales have effectively no excluded volume and are essentially random walks. Thus the factor ϕ^c in Eq. (5.15) is simply the probability that a monomer on a chain be at specified position in the solid, X^{2-d} is the probability that a random walks of blobs starting at some point is at another point a distance X (measured in units of correlation length) away, and finally, $\xi^{\phi/\nu-d}$ is proportional to the density of monomers within a blob.

Arguments similar to the one given above for the correlation functions of monomers on a ring or chain can be given for higher-order correlation functions. The number of constraints on quadrupole operators grows with the number of monomers known to be on any particular polymer or polymer type and thus the number of transverse components which must be considered also grows.

It is, for example, of at least academic interest to inquire whether a magnetic analogy can be given to the situation in which the free energies for adding a monomer to a ring or chain polymer are, in fact, different. This can, in principle, be done by considering an infinite-dimensional quadrupole operator in the Hamiltonian of Eq. (5.1). If we consider the perturbation expansion of Eq. (5.1) with finite g in powers of h, u, and g we will obtain graphs consisting of rings and chains with an arbitrary number of "quadrupole insertions" corresponding to the quadrupole operator, on each ring and chain. In order for this to correspond to a polymer system with equilibrium constant $K_r = \exp(-r_0)$ for adding a monomer to a ring and $K_c = \exp(-r_0 - g)$ for adding a monomer to a chain we require that the presence of any quadrupole insertions on a ring in a graph implies that the graph has value zero. By arguments like those given above it can be seen that the contribution of a graph with m quadrupole insertions is proportional to $\operatorname{tr} Q^m$, the trace of the mth power of the matrix $Q_{\alpha\beta}$. Thus we have an infinite number of conditions; $\operatorname{tr} Q^m = 0$ for $m = 1, 2, \ldots$.

In addition we require that the weight for a chain be given correctly. Again it is straightforward to see that this requires that the one-one component of the mth power of the matrix $Q_{\alpha\beta}$ be unity for all positive m. When this is so the sum of an arbitrary number of quadrupole insertions on a chain polymer with m interactions simply reduces to the product of m geometric series which yields the correct result for the propagator. These two conditions yield an infinite number of conditions which can be satisfied only by considering infinite-dimensional non-Hermitian matrices.

Using infinite-dimensional quadrupole operators it is possible to obtain the length distribution of the polymers, provided the polymers are very long. In particular the sum over all chains in the system of the average of the mth power of the number of monomers in that chain is

$$\langle N_c^m \rangle = m! h^2 \frac{\partial}{\partial h_{\gamma_1} \partial h_{\gamma_m} \partial g Q_{\gamma_1 \gamma_2} \partial g Q_{\gamma_2 \gamma_3} \partial g Q_{\gamma_{m-1} \gamma_m}} \times F(h_\alpha, g Q_{\alpha\beta}) , \tag{5.16}$$

where F is the free energy and $\gamma_1, \gamma_2, \ldots, \gamma_m$ are distinct transverse indices (e.g., unequal to each other and 1). It is clear that the derivative with respect to h_{γ_1} will initiate a labeled chain, the derivatives with respect to the successive gQ's label *ordered* (hence the factor $m!$) monomers on that chain, and finally the derivative with respect the h_{γ_m} ends the chain. This formula is quite general and could be used to calculate the distribution of chain lengths throughout the critical region. Here we will give an example of its use by calculating the distribution in the polymerized phase, i.e., in the ordered magnetic phase, in the limit of low magnetic field.

In this limit we may, to lowest order in the field, approximate the free energy by

$$F(h_\alpha, g Q_{\alpha\beta}) = -\ln \left[\int dM_\alpha \, \delta \left(M_0^2 - \sum_\alpha M_\alpha^2 \right) \times \exp[\mathscr{F}(h_\alpha, g Q_{\alpha\beta})] \right] , \tag{5.17a}$$

with

$$\mathscr{F}(h_\alpha, g Q_{\alpha\beta}) = -V[h_\alpha M_\alpha + g(\phi_c / M_0^2) Q_{\alpha\beta} M_\alpha M_\beta] , \tag{5.17b}$$

where V is the volume, ϕ_c is the chain density in the limit of infinite volume and zero field, and M_0 is the spontaneous magnetization. This is simply the free energy we would obtain if the magnet is viewed as a freely rotating magnet with magnetic moment VM_0. The coupling to the quadrupole operator, which is renormalized by the short-range fluctuations, has been adjusted to give the correct results for the chain density in the infinite-volume limit [Eq. (5.2)]. This approximate free energy does not take proper account of the behavior on short-distance scales. However, it gives the leading behavior when the polymers are very long.

In the limit of large volume ($hM_0 V \gg 1$) and away from the critical region we may approximate the free energy by the minimum of $\mathscr{F}$. Using the method of Langrange multipliers we readily deduce the values for M_α^*, the magnetization which minimizes $\mathscr{F}$,

$$M_\alpha^* = VM_0 \, | h |^{-1} h_\beta [\lambda(Q) \delta_{\alpha\beta} - g \phi_c M_0 \, | h |^{-1} Q_{\alpha\beta}]^{-1} , \tag{5.18}$$

where $| h | = (\sum_\alpha h_\alpha h_\alpha)^{1/2}$, the term in square brackets is to be understood as the *matrix* inverse, and $\lambda(Q) = 1 + O(Q^2)$ must be adjusted so that $\sum_\alpha M_\alpha^{*2} = M_0^2$. From Eqs. (5.16) and (5.18) we readily deduce that

$$\langle N_c^m \rangle = m! VM_0 \, | h | (\phi_c M_0^{-1} | h |^{-1})^m . \tag{5.19}$$

We recognize these moments as being those implied by an exponential distribution of polymer lengths with the average number of polymers given by $| h |^{-1} M_0 V$. The probability that any particular polymer have length N is given by

$$P(N) = M_0 \, | h | \, \phi_c^{-1} \exp(-N M_0^{-1} | h |^{-1} \phi_c) . \tag{5.20}$$

This formula is not correct for (rare) short polymers. Note that it is exactly the mean-field result except for the renormalization of the polymer length.

This simple free energy may also be used to discuss the crossover from chain polymerization to ring polymerization discussed within chemical equilibrium theory in Sec. II. We find very similar results. It is clear that if we have a small system (not connected to other systems by regions the size of a correlation length) in a finite field so that $hM_0V \ll 1$ the free energy of Eq. (5.17) can no longer be approximated by the minimum of $\mathscr{F}$, in particular the average over all possible orientations of the magnetization with the weight given by $\exp(F)$ must be performed. When this is done it is clear that there ceases to be a particular direction in the system and thus the average of quadrupole operators and, in particular, the one which gives the chain density will go to zero. As the total density is unchanged in this limit we conclude that the polymerized density is in large rings.

It is of some interest to ask whether this result has any experimental consequences. Unfortunately, for sulfur the field is probably too large for this to be the case. In particular hM is simply the density of polymer chains in an infinite system. In sulfur this has been measured to be in the range of 10^{-6} per S_8 ring[29] or 10^{-8} Å^{-3}. Thus to observe this effect it would be necessary to disperse the sulfur into regions whose size is of the order of 10^3 Å. Moreover, except very near the transition the correlation length is much less than this, reaching this value at the transition. Thus connections between the regions would have to be appreciably smaller, at most of order 10^2 Å in linear dimension. Care would have to be taken, moreover, that the walls did not produce a sufficiently large effective field (decrease in the free energy of formation of a sulfur radical) to exclude this effect. This conclusion is essentially identical to that reached in Sec. II.

VI. CONCLUSION

In this paper we have examined the equilibrium polymerization of chains and rings together from several different points of view. The common thread running through the various treatments is that the polymerization transition in this system is a confluence of two quite different kinds of critical behavior associated with the rings alone ($n=1$) and chains alone ($n=0$). As such it has aspects of *bicriticality,* and exhibits behavior described by exponents that are present in neither the pure $n=1$ nor pure $n=0$ vector models, but rather are characteristic of the *crossover* between the two in the presence of *quadratic anisotropy.* The two principal results of this paper are, first, that the fraction of monomers in polymeric chains grows above the polymerization temperature T_p as a power law: $\phi_c \sim (T-T_p)^{2-\alpha-\phi}$, where the exponent $2-\alpha-\phi$ is not that describing the total fraction of polymerized monomers, $1-\alpha$, but rather depends upon the crossover exponent, ϕ, for quadratic anisotropy in the n-vector model in the limit $n \rightarrow 1$, and second, that the Hausdorff or fractal dimensionality of chains in the presence of rings is given not by $1/\nu(n=0)$, the result for chains alone, nor by $1/\nu(n=1)$, but rather by $\phi/\nu(n=1)$. In Sec. II we examined the transition in a chemical equilibrium approximation by introducing different polymerization equilibrium constants for chains and rings. This artifice allowed us to distinguish between the transition to infinite rings which occurs in the case when the limit $K_1 \rightarrow 0$ is taken before the limit $V \rightarrow \infty$ and the transition to infinite chains which occurs when the limits are taken in the opposite order. While the exponents obtained in this section are surely in error, the basis notions of a crossover between chains and rings based on the relative magnitudes of V^{-1} and K_1 is surely correct. Sections III–V concern the nonclassical nature of the transition, in particular, the exponents that are expected to describe the various properties and the form of the equation of state for this system. In Sec. III we have shown the correspondence between a lattice model of polymerization that is an extension of that introduced by Cordery[42] and an n-vector model of magnetism. The great advantage of such a map between polymerization and magnetism is that it allows us to make use of the extensive theoretical machinery developed for the study of magnets over the past quarter-century and the vast pool of resulting facts. Lattice models of polymerization such as considered in Sec. III have an advantage over field-theoretic models such as those considered in Secs. IV and V in that they have a well-defined high-density limit in the polymerized phase and lend themselves more naturally to closed-form approximations like mean-field theory. This can be useful in working out approximate phase diagrams. We anticipate that this will be useful in considering the effects of polymeric rings on polymerization in a solvent such as occurs in sulfur solutions. Field-theoretic models, on the other hand, lend themselves more naturally to the powerful calculation techniques of the renormalization-group approach, in particular that of the ϵ expansion. We have taken advantage of this feature together with the magnetic correspondence in Sec. V to obtain the scaling equation of state for equilibrium polymerization of chains in the presence of rings, as well as for chains alone, to lowest order in ϵ in addition to the expected scaling form and estimates for the exponents, which were already available.[34–37,49,50] While the correspondence to magnetism has many advantages, it also imposes limitations upon the physical parameters in the polymeric system. While this can be overcome to some extent by including multispin interactions, as detailed in Appendix B, it is nevertheless of interest to have a calculational method that can be applied directly to the polymer model itself. This is the subject of Sec. IV where we have obtained results to first order in $\epsilon=4-d$ directly on a field-theoretic model of equilibrium polymerization of chains and rings. This gives us the freedom, for example, to consider the effects of making the chain and ring propagation constants K_c and K_r distinct, and thereby allows us to address the question of the shape of the phase diagram in Fig. 1. While quadratic anisotropy of the n-vector model also breaks this symmetry, allowing us to calculate ϕ_c, the correspondence with the polymer model does not hold for nonzero values of the anisotropy field.

It would be of some interest to obtain the first-order scaling function $g(\theta)$ for ϕ_c in Eq. (5.8). Although the singularities near $\theta=1$ (i.e., on the coexistence curve) arising from Goldstone modes for the general n-vector model vanish in the equation of state (m, h, and τ) when $n=1$, we anticipate that remnants of this singularity will remain in $g(\theta)$ even for $n=1$ because ϕ_c arises as a derivative with respect to the symmetry-breaking field. This question is currently under investigation.

The lattice model we have considered in Sec. III is different from that proposed by Helfrich and Müller.[43] It is similar in spirit to that proposed by Cordery.[42] It has the advantage that the excluded volume of polymers is taken into account in an obvious and straightforward manner. Its disadvantage is that the corresponding magnetic model is a modification of the n-vector model. An application of the principle of universality is therefore required in order to identify the exponents of the model with those of the usual n-vector model. As noted in Sec. III, the usual n-vector model can itself be exactly related to a model of equilibrium polymerization of rings and chains. The polymer model then consists of an arbitrary number of monomers, either open or closed, at each lattice site (cell) with an arbitrary number of monomer-monomer bonds on each lattice bond, consistent with the site occupations. The statistical weight of each distinguishable lattice configuration is weighted by $\sqrt{2K_1}$ raised to the power equal to the number of polymer ends, K_p raised to the number of monomer-monomer bonds, $\frac{1}{2}$ to the number of single site "polymers" (active monomers) and, in addition, a factor for each site which depends upon the number of polymers which meet there and is a monotone decreasing function of this number that depends upon n and vanishes as $n \to 0$ for more than one polymer. This is essentially the model proposed by Müller and Helfrich. It has the advantage that it is directly related to the usual n-vector model, but the disadvantage that the weighting of the multiply occupied states in the polymer model is less obviously small enough to give sensible results for high polymer densities (large values of K_p). Nevertheless, we anticipate that this latter model will be useful in generalizations to polymerization in a solvent, where approximate solutions will be of importance.

The subtle dependence of the fractal dimensionality of chains on the absence or presence of rings has been demonstrated only for equilibrium polymerization. To what extent this effect depends upon equilibrium is an interesting question that we have not addressed here. Surely the presence of a fixed distribution of small finite-size rings cannot affect the general $n=0$ result for chains. On the other hand, fixed distributions of both chains and rings that include all sizes might well show similar modification. We expect that the methods developed by Knoll, Schaffer, and Witten[71] for dealing with arbitrary chain length distributions may be useful in addressing these questions.

We have not considered in this paper the effects of rigidity of the polymers. These can be included. For modest rigidity the effect is primarily modification of the probability of forming rings [e.g., the factor B in Eq. (2.1)] and of the effective monomer-monomer interactions. For greater rigidity, interesting liquid-crystalline behavior can result.[72]

While the results obtained for the fraction of material in chains, ϕ_c, and the fractal dimensionality of those chains, D_f, are of considerable theoretical interest, it may be quite difficult to test these predictions experimentally. The exponent characterizing the fractal dimensionality of chains changes by only about 2.5%, and the separation of the fraction of monomers in chains from the total fraction of monomers in polymers presents serious experimental difficulties. We remark that the effects of polymeric rings on the phase diagrams of solutions of monomers undergoing equilibrium polymerization in an inert solvent may show more dramatic effects. Here the presence of rings can lead to qualitatively new phase diagrams and new kinds of higher-order critical points.[73] The polymerization of sulfur in various organic solvents provides interesting practical examples. This will be the subject of a separate publication.

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APPENDIX A

In this appendix we derive the properties of a chemical equilibrium theory of polymerization based on random walks on a lattice. We first introduce some notation and results for random one-step walks on a finite simple-cubic lattice. We then introduce the chemical equilibrium theory and use the random-walk results to solve it. The model and results are slightly different than those in Sec. II because of the presence of the lattice but the essentials are the same.

Consider a finite section of a simple-cubic lattice consisting of L^3 lattice sites $\mathbf{i}=(i_x,i_y,i_z)$ with $i_\alpha=1,2,\ldots,L$. The number $N(\mathbf{i},\mathbf{j},m)$ of random walks with nearest-neighbor steps on this finite lattice from site $\mathbf{i}$ to site $\mathbf{j}$ in exactly m steps satisfies the partial difference equation, for $m \geq 1$,

$$N(\mathbf{i},\mathbf{j},m)=\sum_{\mathbf{j}'}\Delta_{\mathbf{j},\mathbf{j}'}N(\mathbf{i},\mathbf{j}',m-1) \tag{A1}$$

where $\Delta_{\mathbf{j},\mathbf{j}'}$ is unity if $\mathbf{j}$ and $\mathbf{j}'$ are nearest-neighbor sites on the finite lattice and zero otherwise, and the sum over $\mathbf{j}'$ is over all L^3 sites on the finite lattice. The initial condition is given by

$$N(\mathbf{i},\mathbf{j},0)=\delta_{\mathbf{i},\mathbf{j}}\ , \tag{A2}$$

where $\delta_{\mathbf{i},\mathbf{j}}$ is the Kronecker delta function.

The chemical equilibrium model introduced below requires the consideration of the discrete Laplace transform of $N(\mathbf{i},\mathbf{j},m)$:

$$N_{\mathrm{eq}}(\mathbf{i},\mathbf{j},K)\equiv\sum_{m=1}^{\infty}K^m N(i,j,m)\ . \tag{A3}$$

From Eqs. (A1)—(A3) it follows that N_{eq} satisfies the equation

$$N_{\rm eq}(\mathbf{i},\mathbf{j},K)-\sum_{j'}K\Delta_{\mathbf{j},\mathbf{j}'}N_{\rm eq}(i,j',K)=\delta_{ij}\ . \tag{A4}$$

Equation (A4) may be solved in terms of a complete set of eigenfunctions of the operator $\Delta_{\mathbf{i},\mathbf{j}}$. The result is, formally,

$$N_{\rm eq}(\mathbf{i},\mathbf{j},K)=\sum_{\mathbf{k}}u^*(\mathbf{i},\mathbf{k})u(\mathbf{j},\mathbf{k})[1-K\lambda(\mathbf{k})]^{-1}\ , \tag{A5}$$

where $u(\mathbf{i},\mathbf{k})$ satisfies the eigenvalue equation

$$\sum_{j'}\Delta_{\mathbf{j},\mathbf{j}'}u(\mathbf{j}',\mathbf{k})=\lambda(\mathbf{k})u(\mathbf{j},\mathbf{k}) \tag{A6}$$

with the normalization condition

$$\sum_{\mathbf{i}}u^*(\mathbf{i},\mathbf{k})u(\mathbf{i},\mathbf{k}')=\delta_{\mathbf{k}\mathbf{k}'}\ . \tag{A7}$$

It is easily verified that a complete set of orthonormal eigenfunctions for the finite lattice specified above is given by

$$\begin{aligned}u(\mathbf{i},\mathbf{k})=\left[\frac{2}{L+1}\right]^{3/2}&\sin[\pi i_xk_x/(L+1)]\\ &\times\sin[\pi i_yk_y/(L+1)]\\ &\times\sin[\pi i_zk_z/(L+1)]\end{aligned} \tag{A8}$$

with eigenvalues

$$\begin{aligned}\lambda(\mathbf{k})=2\{&\cos[\pi k_x/(L+1)]+\cos[\pi k_y/(L+1)]\\ &+\cos[\pi k_z/(L+1)]\}\ ,\end{aligned} \tag{A9}$$

where k_x,k_y,k_z run from 1 to L.

Now consider a simple equilibrium theory for the polymerization of chains and rings. Let x_0 and x_{mc} be the concentrations of inactive monomers and of polymer chains, respectively, expressed as the number of the objects of interest divided by the total number of monomers in all forms. Let them be related, for $m\geq 1$, by

$$x_{mc}=K_1x_0L^{-3}\sum_{\mathbf{i}}\sum_{\mathbf{j}}N(\mathbf{i},\mathbf{j},m-1)(K_c'x_0)^{m-1}\ . \tag{A10}$$

According to Eq. (A2) this gives

$$x_{1c}\equiv K_1x_0 \tag{A11}$$

and, for fixed m, as $L\rightarrow\infty$, gives

$$x_{mc}=K_1x_0(K_cx_0)^{m-1}\ , \tag{A12}$$

where

$$K_c=6K_c'\ . \tag{A13}$$

This follows from the fact that the total number of random walks of length m from a typical interior site on an infinite simple cubic lattice is 6^m. Equation (A12) for $m\geq 2$ is equivalent to the Tobolsky-Eisenberg theory for equilibrium polymerization of chains. Equation (A10) amounts to associating a polymer chain with each random walk on the lattice. No excluded-volume effects are included.

For rings of m monomers, the corresponding concentration x_{mr} is taken to be

$$x_{mr}=(2m)^{-1}L^{-3}\sum_{\mathbf{i}}N(\mathbf{i},\mathbf{i},m)(K_r'x_0)^m\ . \tag{A14}$$

Here K_r' plays the role of a statistical weight for a ring bond and closed walks on the lattice are associated with polymer rings. The factor $(2m)^{-1}$ compensates for the overcounting of loops resulting from the fact that the same loop is generated as a closed walk starting in either direction at each of the sites that it occupies. It is a feature of the simple cubic lattice that

$$N(\mathbf{i},\mathbf{i},m)=0\quad(m\ \text{odd})\ . \tag{A15}$$

For even loops, $N(i,i,2m)$ is easily expressed by direct counting in the form

$$N(\mathbf{i},\mathbf{i},2m)=\sum_{m_1}\sum_{m_2}\frac{(2m)!}{(m_1!)^2(m_2!)^2[(m-m_1-m_2)!]^2}\ , \tag{A16}$$

provided site $\mathbf{i}$ is more than m steps removed from any boundary, and where the sums on m_1 and m_2 are over integers such that m_1, m_2, and $m-m_1-m_2$ are all nonnegative. For fixed m, as $L\rightarrow\infty$, x_{mr} approaches a well-defined limit. For large m this is easily shown to be of the form (for m even)

$$x_{mr}\sim Bm^{-2/5}(K_rx_0)^m \tag{A17}$$

with

$$K_r=6K_r' \tag{A18}$$

and

$$B=(3/2\pi)^{-1/2}\ . \tag{A19}$$

The total concentrations of chains and rings x_c and x_r and the fractions of monomers in chains and rings, ϕ_c and ϕ_r, are defined by

$$\begin{aligned}x_c&=\sum_{m=1}^{\infty}x_{mc},\quad x_r=\sum_{m=1}^{\infty}x_{mr}\ ,\\ \phi_c&=\sum_{m=1}^{\infty}mx_{mc},\quad \phi_r=\sum_{m=1}^{\infty}mx_{mr}\ .\end{aligned} \tag{A20}$$

(The terms with $m=1$ in x_r and ϕ_r contribute nothing to the sums, but are retained for convenience in evaluation.)

From Eqs. (A3)—(A7) they are found to be

$$\begin{aligned}x_c(K_c')=(K_1x_0)L^{-3}\sum_{\mathbf{k}}&\left|\sum_{\mathbf{i}}u(\mathbf{i},\mathbf{k})\right|^2\\ &\times[1-K_c'x_0\lambda(\mathbf{k})]^{-1}\ ,\end{aligned} \tag{A21}$$

$$x_r(K_r')=\tfrac{1}{2}L^{-3}\sum_{\mathbf{k}}\ln[1-K_r'x_0\lambda(\mathbf{k})]\ , \tag{A22}$$

$$\begin{aligned}\phi_c(K_c')=(K_1x_0)L^{-3}\sum_{\mathbf{k}}&\left|\sum_{\mathbf{i}}u(\mathbf{i},\mathbf{k})\right|^2\\ &\times[1-K_c'x_0\lambda(\mathbf{k})]^{-2}\ ,\end{aligned} \tag{A23}$$

$$\phi_r(K_r')=\tfrac{1}{2}L^{-3}\sum_{\mathbf{k}}\frac{K_r'x_0\lambda(\mathbf{k})}{1-K_r'x_0\lambda(\mathbf{k})}\ . \tag{A24}$$

They satisfy the conservation equation

$$1=x_0+\phi_r+\phi_c\ . \tag{A25}$$

Using Eq. (A8) one finds for $\sum_{\mathbf{i}} u(\mathbf{i},\mathbf{k})$,

$$\sum_{\mathbf{i}} u(\mathbf{i},\mathbf{k})=\left[\frac{2}{L+1}\right]^{3/2}\cot\left[\frac{\frac{1}{2}\pi k_x}{L+1}\right]\cot\left[\frac{\frac{1}{2}\pi k_y}{L+1}\right]\times\cot\left[\frac{\frac{1}{2}\pi k_z}{L+1}\right] \tag{A26}$$

when k_x, k_y, and k_z are all odd integers, and identically zero whenever any one of k_x,k_y,k_z is even. We thus obtain for x_c

$$x_c=K_1x_0L^{-3}8(L+1)^{-3}\times\sum_{\mathbf{k}}{}'[1-K_cx_0\lambda(\mathbf{k})]^{-1}\cot^2\left[\frac{\pi k_x}{2(L+1)}\right]\times\cot^2\left[\frac{\pi k_y}{2(L+1)}\right]\cot^2\left[\frac{\pi k_z}{2(L+1)}\right], \tag{A27}$$

where the sum $\sum'_{\mathbf{k}}$ is over all odd k_x,k_y,k_z from 1 to L, and similarly for ϕ_c with $[1-K_cx_0\lambda(\mathbf{k})]^{-1}$ replaced by $[1-K_cx_0\lambda(\mathbf{k})]^{-2}$. As $L\to\infty$, x_c and ϕ_c are dominated by the low-$\mathbf{k}$ contributions so that $\lambda(\mathbf{k})$ can be replaced by 6 and $\cot^2[\pi k/2(L+1)]$ can be replaced by $[2(L+1)/\pi k]^2$. The result is

$$x_c=\frac{K_1x_0}{1-K_cx_0}\left[\frac{L+1}{L}\right]^3\left[\frac{8}{\pi^2}\sum_k{}'\frac{1}{k^2}\right]^3, \tag{A28}$$

where the sum is over odd k from 1. The sum is easily evaluated to give

$$\sum_k{}'k^{-2}=\tfrac{3}{4}\zeta(2)=\frac{\pi^2}{8} \tag{A29}$$

so that

$$x_c=\frac{K_1x_0}{1-K_cx_0}[1+O(L^{-1})]\ . \tag{A30}$$

Similarly

$$\phi_c=\frac{K_1x_0}{(1-K_cx_0)^2}[1+O(L^{-2})]\ . \tag{A31}$$

These are precisely the Tobolsky-Eisenberg results.

Consider next the behavior of x_r and ϕ_r when $K_rx_0\le 1$, which holds in the interior of regions I and II. Then the expressions for x_r and ϕ_r in (A22) and (A24) can be expanded in powers of $K_r'x_0$ with the result

$$x_r=\tfrac{1}{2}\sum_{m=1}^{\infty}m^{-1}(K_r'x_0)^mL^{-3}\sum_{\mathbf{k}}[\lambda(\mathbf{k})]^m\ ,$$

$$\phi_r=\tfrac{1}{2}\sum_{m=1}^{\infty}(K_r'x_0)^mL^{-3}\sum_{\mathbf{k}}[\lambda(\mathbf{k})]^m\ . \tag{A32}$$

Comparison with Eqs. (A14) and (A20) [or of (A3) and (A5)] gives

$$\sum_{\mathbf{i}}N(\mathbf{i},\mathbf{i},m)=\sum_{\mathbf{k}}[\lambda(\mathbf{k})]^m\ . \tag{A33}$$

The symmetry property

$$\sum_{\mathbf{k}}[\lambda(\mathbf{k})]^{2m+1}=0 \tag{A34}$$

of the eigenvalues in (A9) implies Eq. (A15). For even rings, one finds, as $L\to\infty$, both by expansion of (A33) and by direct counting walks [cf. (A16)], that

$$L^{-3}\sum_{\mathbf{i}}N(\mathbf{i},\mathbf{i},2m)=\sum_{m_1}\sum_{m_2}\frac{(2m)!}{(m_1!)^2(m_2!)^2[(m-m_1-m_2)!]^2}\ , \tag{A35}$$

where the sum on m_1 and m_2 is as in Eq. (A16). For large m, an asymptotic expansion about the maximum term in (A35), for which $m_1=m_2\approx m/3$, gives

$$L^{-3}\sum_{\mathbf{i}}N(\mathbf{i},\mathbf{i},2m)\approx 2^{-1/2}(3/\pi)^{3/2}(2m)^{-3/2}6^{2m}\ , \tag{A36}$$

which implies (A17)–(A19). The fact that x_{mr} is zero for odd m and approaches the form in (2.1) only for large m may be viewed either as an approximation in the equations of Sec. II or as an artificiality of the cubic lattice model employed here. While it changes the numerical values of K_r^c and x_0^c it does not change any of the qualitative conclusions.

The calculation of x_r and ϕ_r in region III requires somewhat more care. The low-k terms do not dominate the sums in (A22) and (A24), and, moreover, the sums converge even when $K_rx_0=1$. As a consequence, the lowest eigenvalue plays a special role analogous to the quantum ground state in the ideal Bose gas. As K_rx_0 approaches $1+\frac{1}{2}[\pi/(L+1)]^2$ to within of order L^{-3}, the term $k_x=k_y=k_z=1$ in the sum for ϕ_r [Eq. (A24)] is of order 1 so that the conservation equation can be satisfied. The remaining terms, however, can still be approximated by an integral, with $K_rx_0=1$. Thus, for large L we then have

$$x_r\cong\tfrac{1}{2}L^{-3}\ln\left[1-K_rx_0\cos\left[\frac{\pi}{L+1}\right]\right]+\frac{1}{2\pi^3}\int_{\pi/(L+1)}^{\pi}dk_1\int_{\pi/(L+1)}^{\pi}dk_2\int_{\pi/(L+1)}^{\pi}dk_3\ln\left[1-K_rx_0\left[\frac{\cos k_1+\cos k_2+\cos k_3}{3}\right]\right], \tag{A37}$$

$$\phi_r \cong \tfrac{1}{2} L^{-3} \frac{(K_r x_0)\cos[\pi/(L+1)]}{1-K_r x_0 \cos[\pi/(L+1)]} + \frac{1}{2\pi^3} \int_{2\pi/(L+1)}^{\pi} dk_1 \int_{2\pi/(L+1)}^{\pi} dk_2 \int_{2\pi/(L+1)}^{\pi} dk_3 \left[\frac{\frac{1}{3} K_r x_0 (\cos k_1 + \cos k_2 + \cos k_3)}{1-\frac{1}{3} K_r x_0 (\cos k_1 + \cos k_2 + \cos k_3)} \right] . \tag{A38}$$

The first term in x_r varies as $L^{-3}\ln L$ so that the total number of rings of the size of the system varies as

$$(N_{r\infty}^{L} \sim \ln L) . \tag{A39}$$

From Eq. (A32), x_{mr} can be expressed as

$$x_{mr} = (2m)^{-1}(K_r x_0)^m L^{-3} \sum_{\mathbf{k}} [\lambda(\mathbf{k})]^m . \tag{A40}$$

For m very large, specifically, large compared to $[\pi/(L+1)]^{-2}$, the sum on k is dominated by the terms with $k_x = k_y = k_z = 1$ and L. Thus (for m even)

$$x_{mr} = (m)^{-1}(K_r x_0)^m L^{-3} \left[\cos \left[\frac{\pi}{L+1} \right] \right]^m \times (1 + \text{smaller terms}) \tag{A41}$$

we can express this in the form

$$x_{mr} = (m)^{-1}(K_r x_0)^m L^{-3} e^{-[f(l)]m} , \tag{A42}$$

where

$$f(l) = -\ln \left[\cos \left[\frac{\pi}{L+1} \right] \right] \approx \frac{1}{2} \left[\frac{\pi}{L+1} \right]^2 . \tag{A43}$$

This is precisely the form for large rings quoted in Sec. II.

It is interesting to note that in two or fewer dimensions the sums in (A22) and (A24) are not completely dominated by the ground state. Rather, the sums diverge for $K_r x_0 \to 1$ so that no condensation of infinite rings results, and no transition involving only rings takes place. This is intimately related to the absence of Bose-Einstein transition in the ideal Bose gas in two dimensions.

APPENDIX B

In this appendix we demonstrate an exact correspondence between a simple model of equilibrium polymerization with rings and a magnetic model. Correspondences between the long-distance behavior of magnetic and polymer systems have been demonstrated in Sec. III of this paper and elsewhere.[38-51,55] Two approaches have been used. Lattice models involve a periodic substrate which also builds in artificial short-distance behavior. In simple field-theoretic correspondences with magnets, there are difficulties and artificialities associated with the treatment of the short-wavelength cutoff, particularly if rings are allowed. In this appendix these potential difficulties are avoided by using an explicit, reasonably realistic model for the polymers. This allows a discussion of when the behavior of realistic systems can depart from that discussed above.

In demonstrating this correspondence we give a treatment of the Usrell-Mayer expansion of the polymer system. We consider a system of freely jointed polymer chains and rings in equilibrium whose monomers interact via a potential V. In order to specify such a system we must give the statistical weights of the polymer species in the absence of interactions, i.e., probabilities for any conformation of an individual polymer in the absence of interactions between monomers, and also the interaction potential between monomers which are included in polymers.

We assume that the polymers are freely jointed, i.e., that the noninteracting statistical weight for an m-mer with an end fixed at $\mathbf{x}_1$ in the configuration with the $(i-1)$th monomer from this end at position $\mathbf{x}_i$, is

$$S_c(m,\{\mathbf{x}\}) = K_1 K_p, \quad m = 1 \tag{B1a}$$

$$= 2K_1 K_p^m \prod_{i=1}^{m-1} P(|\mathbf{x}_i - \mathbf{x}_{i+1}|), \quad m \neq 1 \tag{B1b}$$

where $P(x)$ is normalized $[\int d\mathbf{x} P(|\mathbf{x}|) = 1]$ and describes the bond length distribution. For reasons discussed below we will require the natural condition $P(|\mathbf{x}|=0)=0$. Note that this definition of K_1 differs from that given in Sec. II by a factor of K_p. We assume that statistical weight of rings is such that bonds in rings are indistinguishable from bonds in chains. This implies that the statistical weight of an m-member ring with m distinguishable monomers at $\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_m$ is

$$S_r(m,\{\mathbf{x}\}) = \begin{cases} 0, \quad m = 1 & \text{(B2a)} \\ \frac{1}{2} P(|\mathbf{x}_1 - \mathbf{x}_2|)^2, \quad m = 2 & \text{(B2b)} \\ P(|\mathbf{x}_1 - \mathbf{x}_m|) \prod_i P(|\mathbf{x}_i - \mathbf{x}_{i+1}|), \quad m \geq 3 . & \end{cases} \tag{B2c}$$

The factors of 2 and $\frac{1}{2}$ in Eqs. (B1b) and (B2) are required for a simple correspondence to the magnet and can be justified physically as being associated with the indistinguishability of bonds and monomers.

We will assume that *all* monomers in polymers of all types interact via the two-body potential $V(|\mathbf{x}|)$. In an actual system (e.g., sulfur) this potential should should be thought of as the interaction potential between monomers in polymers mediated by inactive monomers or other solvents. This defines the system under consideration. More complex (many-body) interactions are a trivial extension.

The grand canonical partition function for an interacting system of this nature is given by

$$e^{-PV/k_BT}=1+\sum_{N=1}^{\infty}\frac{1}{N!}\sum_{\text{partitions}}\int d\mathbf{x}_1\int\cdots\int d\mathbf{x}_N\left[\prod_{i=1}^{N_r}S_r(m_i^r,\{\mathbf{x}\})\right]\left[\prod_{j=1}^{N_c}S_c(m_j^c,\{\mathbf{x}\})\right]\exp\left[-\tfrac{1}{2}\sum_{i,j=1}^{N}V(\mathbf{x}_i-\mathbf{x}_j)/k_BT\right], \tag{B3}$$

where k_B is Boltzmann's constant, T is the temperature, V is the volume, P is the (osmotic) pressure, N is the number of polymerized monomers in a given realization of the ensemble, and the sum over partitions is a sum over all possible ways of partitioning these N monomers into an arbitrary number, N_r, of ring polymers containing arbitrary numbers $m_1^r,m_1^r,\ldots,m_{N_r}^r$ of monomers and an arbitrary number, N_c, of chain polymers containing arbitrary numbers $m_1^c,m_2^c,\ldots,m_{N_c}^c$ of monomers. When either N_r or N_c is zero the product involving it should be replaced by unity.

We may calculate the properties of such a system perturbatively within an Ursell-Mayer expansion. This expansion may be represented pictorially in a system with this complex molecular nature[64] as well as in the more familiar case in which the noninteracting system consists of point particles.[62] In particular, instead of graphs consisting of point particles and interaction lines we must draw graphs consisting of polymers and interaction lines. The rules for drawing interaction lines between monomers are identical to those for the particle system, e.g., at most one interaction line between each monomer pair. If we wish to calculate the density of monomers, or densities of or correlations between monomers with certain properties, we must distinguish these monomers from other monomers.

The value of a graph is calculated as follows. Associate a position $\mathbf{x}_i$ with each polymerized monomer in a graph. Integrate over the positions of all monomers (except those which have been distinguished as having a certain position) the product of (a) the noninteracting statistical weight of all polymers in the graph, (b) the product of $f(|\mathbf{x}_i-\mathbf{x}_i'|)$ over all pairs of monomers connected by interaction lines where $f(|\mathbf{x}|)=\exp[-V(|\mathbf{x}|)/k_BT]-1$ is the Mayer f function, and (c) the inverse of any symmetry factor of the graph, i.e., the inverse of the number of ways in which polymerized monomers may be interchanged leaving the topology of the graph fixed. In order to calculate a quantity we sum over all possible graphs the value of each graph. In particular, the (osmotic) pressure $-PV/k_BT$ is given by the sum of all connected graphs, the number of polymerized monomers is given by the sum of all connected graphs with a single distinguished monomer which has its position integrated over space, etc.

In performing the sum over graphs at any order in the interaction f we must sum over the possibility that there are any arbitrary number of monomers between monomers with interactions, between monomers with interactions and distinguished monomers, or between such monomers and the ends of polymer chains. This motivates the consideration of the sum

$$G(|\mathbf{x}-\mathbf{x}'|)=P(|\mathbf{x}-\mathbf{x}'|)+\sum_{l=1}^{\infty}\int d\mathbf{x}_1\int\cdots\int d\mathbf{x}_l\,K_p^lP(|\mathbf{x}-\mathbf{x}_1|)P(|\mathbf{x}'-\mathbf{x}_l|)\prod_{j=1}^{l-1}P(|\mathbf{x}_j-\mathbf{x}_{j+1}|)\,, \tag{B4}$$

where the $\mathbf{x}_i$ are the positions of intervening monomers and if $l=1$ the product is to be replaced by unity. We now consider graphs in which bonds (or dangling bonds) and the pieces of polymer described above are replaced by solid lines (see, e.g., Fig. 5) with the following rules for evaluation. Associate a position x_i and a factor K_p with each (distinguished or interacting) monomer in such a graph, $G(|\mathbf{x}-\mathbf{x}'|)$ with each solid line (polymer segment), and $f(|\mathbf{x}-\mathbf{x}'|)$ with each dashed (interaction) line. Associate a factor $(2K_1)^{1/2}$ and a position with the "end" of a polymer chain [actually with the position of a bond dangling from the last monomer on a chain, i.e., a position $\mathbf{x}_b$ whose distribution from the position of the last monomer on the chain, $\mathbf{x}_f$, is given by $P(|\mathbf{x}_b-\mathbf{x}_f|)$]. Associate a symmetry factor with the graph given by the number of ways solid lines and interacting or distinguished monomers can be interchanged without changing the topology or meaning of the graph. If we then integrate over the positions of interacting monomers and the ends of polymer chains we readily verify that all graphs (except those containing polymers with neither interacting nor distinguished monomers) have values equal (order by order in perturbation theory) to the sum of the primitive Ursell-Mayer graphs. Note that the statistical factors of 2 and $\frac{1}{2}$ appearing in Eqs. (B1) and (B2) are necessary to these simple graphical rules. Note also that unless we require that $P(|\mathbf{x}|=0)=0$ these rules yield spurious contributions from loops of solid lines with exactly one distinguished or interacting monomer.

The sum of disconnected parts of graphs containing neither interacting nor distinguished monomers must be calculated separately. For chain polymers the sum is

$$\begin{aligned}\Sigma_0^c&=K_1K_p\int d\mathbf{x}_1\\&\quad+\sum_{l=2}^{\infty}K_1K_p^l\int d\mathbf{x}_1\int\cdots\int d\mathbf{x}_l\prod_{j=1}^{l-1}P(|\mathbf{x}_j-\mathbf{x}_{j+1}|)\\&=VK_1K_p/(1-K_p)\,.\end{aligned} \tag{B5}$$

For ring polymers this sum is

$$\Sigma_0^r=\sum_{l=2}^{\infty}\frac{1}{2l}\int d\mathbf{x}_1\int\cdots\int d\mathbf{x}_l K_p^l P(|\mathbf{x}_1-\mathbf{x}_l|)\times\sum_{j=1}^{l-1}P(|\mathbf{x}_j-\mathbf{x}_{j+1}|)$$

$$=\frac{V}{2}\int\frac{d\mathbf{k}}{(2\pi)^d}\ln[1-K_p\widetilde{P}(|\mathbf{k}|)]\ , \tag{B6}$$

where

$$\widetilde{P}(k)=\int d\mathbf{x}\, e^{i\mathbf{k}\cdot\mathbf{x}}P(|\mathbf{x}|)\ .$$

The right-hand side has been Fourier transformed and summed. Use has been made of the fact $\int d\mathbf{k}\widetilde{P}(|\mathbf{k}|)=\widetilde{P}(|\mathbf{x}|=0)\equiv 0$. The sum of Eq. (B4) can also easily be evaluated yielding

$$G(|\mathbf{x}-\mathbf{x}'|)=\int\frac{d\mathbf{k}}{(2\pi)^d}\widetilde{P}(|\mathbf{k}|)[1-K_p\widetilde{P}(|\mathbf{k}|)]^{-1}\ . \tag{B7}$$

We note that these sums will diverge if $K_p>1$ as $\widetilde{P}(k)\le 1$ achieves the limit $\widetilde{P}(k)=1$ when $k=0$. Thus this naive perturbation theory will diverge for $K_p>1$. This is due to the instability of the reference state when $K_p>1$ and can be corrected by use of a more appropriate reference state as discussed in Sec. IV.

As has been remarked, the graphs obtained in this way bear a close resemblance to those obtained in expansions of magnetic problems. In particular consider an n-component magnet with the energy $H/k_BT=\widetilde{H}_0+\widetilde{H}_1$,

$$\widetilde{H}_0=\int d\mathbf{x}\int d\mathbf{x}'\,\tfrac{1}{2}\phi(\mathbf{x})\phi(\mathbf{x}')\mathscr{K}(|\mathbf{x}-\mathbf{x}'|)\ , \tag{B8a}$$

$$\widetilde{H}_1=-\int h\phi(\mathbf{x})d\mathbf{x}-\sum_{j=2}^{\infty}\int d\mathbf{x}_1\int\cdots\int d\mathbf{x}_j(K_p/2)^j(j!)^{-1}\times U_j(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_j)\times\prod_{j'=1}^{j}[\phi(\mathbf{x}_{j'})]^2\ . \tag{B8b}$$

We define the free energy of this system in the usual way by a functional integral

$$-VF/k_BT=\ln\left[\int(\mathscr{D}\phi)\exp(-H/k_BT)\right] \tag{B9}$$

and expectation value of a function A depending on the field ϕ by

$$\langle A(\phi)\rangle=\int(\mathscr{D}\phi)\exp[-(H/k_BT)+(VF/k_BT)]A(\phi)\ . \tag{B10}$$

We will show that if the parameters are picked correctly this magnetic system corresponds to the polymer system order by order in perturbation theory. In particular we will show that

$$-P/k_BT=-(F/k_BT)+K_1+C\ , \tag{B11}$$

where P is the (osmotic) pressure defined by Eq. (B3), F is the free energy of the magnet defined by Eq. (B9), and C is a constant. We will also show that there is a correspondence between expectation values calculated in the two systems.

For this correspondence we require $h^2=2K_1$,

$$\mathscr{K}(|\mathbf{x}|)=\frac{1}{(2\pi)^d}\int d\mathbf{k}\,e^{i\mathbf{k}\cdot\mathbf{x}}\{[\widetilde{P}(k)]^{-1}-K_p\} \tag{B12}$$

and that U_j is given by the jth Ursell cluster function[62] for the interaction potential $V(|\mathbf{x}|)$, i.e.,

$$\begin{aligned}U_2(\mathbf{x}_1,\mathbf{x}_2)&=f(|\mathbf{x}_1-\mathbf{x}_2|)\ ,\\ U_3(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3)&=f(|\mathbf{x}_1-\mathbf{x}_2|)f(|\mathbf{x}_2-\mathbf{x}_3|)+f(|\mathbf{x}_3-\mathbf{x}_1|)f(|\mathbf{x}_3-\mathbf{x}_2|)+f(|\mathbf{x}_2-\mathbf{x}_1|)f(|\mathbf{x}_2-\mathbf{x}_3|)\\ &\quad+f(|\mathbf{x}_1-\mathbf{x}_2|)f(|\mathbf{x}_2-\mathbf{x}_3|)f(|\mathbf{x}_1-\mathbf{x}_3|)\ ,\end{aligned} \tag{B13}$$

and so forth.

To demonstrate this correspondence we expand the magnet problem in a perturbation theory in $\widetilde{H}_1$ in the standard (Wick ordering) fashion.[74] The free energy is then F_0, the free energy for the unperturbed Hamiltonian, plus the sum of all connected graphs. This unperturbed free energy is given by

$$-VK_0/k_BT=\frac{V}{2}\int\mathrm{Tr}\ln[\mathscr{K}(\mathbf{x}-\mathbf{x}')]$$

$$=\Sigma_0^r-\frac{V}{2}\int\frac{d\mathbf{k}}{(2\pi)^d}\ln[\widetilde{P}(\mathbf{k})]\ , \tag{B14}$$

where Σ_0^r is given by Eq. (B6) and the remainder is the constant C. We note that this constant, which in any case is irrelevant to the thermodynamics, will be finite only if $\widetilde{P}(k)$ tends to zero as $k\to\infty$ more rapidly than $\exp(-ak^d)$ for any a. It is easy to verify that the connected graphs for this magnet are identical to the connected graphs obtained by summing over intervening monomers in the polymer system (exclusive of the sum over noninteracting polymers). Such graphs would involve the propagator for the magnetic system, which equals $G(|\mathbf{x}|)$ given in Eq. (B4); field vertices which have associated with them a factor h, a position to be integrated over, and one propagation line; and j-fold interactions which have associated with them a factor $2^{-j}(j!)K_p^jU_j(\mathbf{x}_1,\ldots,\mathbf{x}_j)$, j positions $\mathbf{x}_i$ to be integrated over, and $2j$ propagation lines which meet in pairs at the j positions. The factor h accounts for the statistical weight of a polymer end, the factor $K_p^j U_j$ gives the correct statistical weight for j interacting monomers, and the remaining factor $2^{-j}(j!)^{-1}$ is needed because there are a number of Wick orderings (with identical values) corresponding to each polymer configuration. If each of the $2j$ polymer branches (propagators) entering a vertex is distinguishable there are $2^j j!$ different Wick orderings corresponding to each distinct polymer interpretion. If the polymer branches entering the vertex are not distinguishable the number of different Wick orderings multiplied by the factor $2^{-j}(j!)^{-1}$ yields the reciprocal of the symmetry factor discussed for the polymer graphs. Thus if we associate field vertices with the ends of polymers and j-fold interaction vertices with the sum over all possible (connected) ways for clusters of j monomers to interact we see that the graphs obtained from the magnet system equal those obtained above by summing the polymer graphs. The graph proportional to h^2, i.e., the one corresponding to a single polymer chain with no interactions, has the value $h^2\int d\mathbf{x}\, G(\mathbf{x})$. This differs from the correct sum [Eq. (B5)] in the polymer system by VK_1. This difference, Eq. (B14) above and the equality between the connected graphs involving interactions, demonstrates the equivalence between the polymer model and the magnet expressed in Eq. (B11).

It is also easy to verify that the graphs for the calculation of expectation values for certain operators in the magnetic system exactly equal those for certain corresponding expectation values in the Ursell-Mayer expansion. A particular example is the graphs for $\langle K_p \partial(\tilde{H}_0+\tilde{H}_1)/\partial K_p \rangle$ which are the graphs for the total number of polymerized monomers.

It is clear that if we replace ϕ by an n-component vector and take the formal limit $n \rightarrow 0$ we will obtain magnetic perturbation rules appropriate to an equilibrium polymerization problem in which rings cannot be formed.

It is of some interest to inquire whether there are situations in which the magnetic system falls into a universality class other than the ordinary $n=1$ critical point. It is evident that, in the absence of interactions, the maximum in the susceptibility of the magnet, given by the Fourier transform of $G(|\mathbf{x}|)$ defined in Eq. (B4), is at $k=0$. Moreover, it is clear this is a simple maximum. Thus, it is difficult to see how the system can have a Lifschitz point or an order parameter with nonzero wave vector.

On the other hand, it is far from clear that the infinite sum of Eq. (B8b) has the same behavior as the short-range quadratic form used in Eq. (5.1b). For some choices of the Mayer f function it may have only short-ranged contributions but with higher-order minima leading to multicritical behavior.[56,65,25] It is also possible that this infinite sum, which closely resembles that for the pressure of a gas, should have a long-range nature, like that of a gas near its critical point. This would yield yet different behavior.

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