

Parametric equation of state for the n -vector model and polymers

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We introduce a new parametric form for the scaling equation of state of the n -vector model of magnetism correct to first order in $\epsilon=4-d$. It is based on the equation of state of Schäfer and Horner in a general parametric form proposed earlier by Schofield, Litster, and Ho. We integrate it to obtain the scaling part of the free energy $F(T,H)$ of the n -vector model, correct to order ϵ , for general n . We use it to discuss the behavior of polymer solutions and equilibrium polymerization. This equation of state of the $n < 1$ vector model shows no evidence of nonanalyticities in the H - T plane except at the critical point and on the coexistence curve, in disagreement with Gujrati's claim for a singularity at $H > 0$, $T < T_c$ which he interprets as signaling a "collapsed" phase for polymers in the limit $n \rightarrow 0$. We address several of the specific arguments of Gujrati which he uses to support his claim for this singularity. We also discuss the effect of the order of the limits $n \rightarrow 0$, $H \rightarrow 0$, and $V \rightarrow \infty$ on the nature of the polymerized state in equilibrium polymerization.

I. INTRODUCTION

The $O(n)$ vector model of magnetism for $n < 1$, and in particular in the limit $n \rightarrow 0$, has been used extensively to study the properties of polymers and polymer solutions, providing a model for the study of a single polymer in a good solvent,¹ of polymer solutions²⁻⁶ and their scaling properties from the dilute to the semidilute limit and of equilibrium polymerization⁷⁻¹¹ of chains from monomers, both neat and in solution.¹² It has provided a starting point for more general treatments of polymer solutions in which the degree of polydispersity^{4,13} and goodness of solvent¹⁴ are adjustable parameters. An extensive lore has resulted concerning the crossover from dilute to semidilute limits including the concepts of swelling in the dilute limit,¹ screening in the semidilute limit² and the "blob" model¹⁵ of polymers in the semidilute limit.

Recently, these results have been called into question by Gujrati,^{16,17} who has argued that results for the $O(n)$ vector model in the thermodynamic limit cannot be analytically continued below $n = 1$, the smallest value of n for which it can be realized as a magnet. He maintains that the equation of state of the $O(n)$ vector model for $n < 1$ contains a singularity along a locus in the H - T plane that passes through the magnetic critical point and that this singularity corresponds to a physical transition in the polymer system to a "collapsed" state that precludes the usual picture of the semidilute limit as a collection of interpenetrating polymers. This conclusion would be of considerable importance, if true, in view of the extensive use noted above of the $n \rightarrow 0$ vector model as a model of polymer solutions and equilibrium polymerization. It is even more interesting because the $O(n)$ vector model for

positive integer n can be interpreted as a model of equilibrium polymerization in which polymeric rings¹⁸⁻²² as well as chains are in thermal and chemical equilibrium with monomers. Moreover, for positive, noninteger n , it can be interpreted as a polymer solution of polymeric chains and polymeric rings in which a particular relation between activities and statistical weights of various polymer species is satisfied. Thus, Gujrati's claim that the $O(n)$ vector model leads to qualitatively different results for the ordered (polymerized) phase in the corresponding polymer solution according to whether $n \geq 1$ or $n < 1$ implies that the behavior of an equilibrium polymerization system changes radically when rings can form. This seems counterintuitive given that such systems in the polymerized phase contain many chains¹¹ as well as rings. In addition, it implies that an infinitesimal change in the activity of rings drastically changes the behavior of the polymer solution for noninteger n near $n = 1$, again a counterintuitive result. However, we do not agree with the analysis of this author, and believe that no such qualitative difference has been demonstrated.

Gujrati's arguments concerning the equation of state of the n -vector model fall into two distinct categories. In Secs. II-IV he gives a variety of arguments that a direct statistical mechanical calculation of the partition function as a functional integral encounters difficulties when $n < 1$. In Sec. V he argues that published equations of state for the n -vector model cannot be continued to $n < 1$. While we do not agree with the details of the arguments in Secs. II-IV, we will not comment on them here except for two observations. First, the difficulties encountered by Gujrati depend essentially on the lack of thermodynamic stability of states of the $O(n < 1)$ model interpreted as a mag-

net. It is known²³ that the $O(n < 1)$ vector model has negative susceptibility in the ordered phase for sufficiently small field, and this is not consistent with thermodynamic stability. However, there is no inconsistency with the thermodynamic stability of the corresponding polymer system, and, in fact, the negative susceptibility can be understood physically as a “correlation hole” effect in the polymer interpretation. Given the negative susceptibility of the $n < 1$ vector model, it should not be surprising that other magnetic quantities that are expected to be positive are not, or that there are difficulties in interpreting the partition sum directly as a functional integral. We discuss this further in Sec. V. Secondly, however, we emphasize that such difficulties in no way imply that there will be difficulties in continuing the equation of state for the n -vector model, obtained for $n \geq 1$, to $n < 1$.

We disagree with Gujrati’s conclusion in Sec. V that the equations of state of Lawrie²⁴ and of Schäfer and Horner²⁵ cannot be continued to $n < 1$. We will show that the equation of state of Schäfer and Horner²⁵ (SH) can be put into a particularly transparent parametric form first suggested by Schofield, Litster, and Ho²⁶ (SLH). When this is done it becomes clear that there is no difficulty in continuing the equation of state to $n < 1$ throughout the H - T plane excepting only the coexistence curve itself, and that no nonanalyticity arises. Gujrati’s conclusion that Lawrie’s equation of state does not possess a solution for $n < 1$ and sufficiently small field when $T < T_c$, depends upon his argument below his Eq. (32) that the susceptibility must be positive for $H \rightarrow 0$ and $T < T_c$ sufficiently close to T_c . We show below that this is neither logically required nor in fact the case. The parametric equation of state given below satisfies the conditions of Gujrati’s argument but not its conclusions, thus serving as a counterexample to his argument. Other simpler counterexamples are also given. This eliminates the contradiction claimed by Gujrati in Lawrie’s equation of state.

An outline of the rest of this paper is as follows. We first give the SLH parametric form of the equation of state of SH and discuss its properties. We then integrate to obtain the scaling part of the free energy to first order in ϵ . This demonstrates that the free energy of the $n < 1$ vector model exists, and is analytic except at $h = 0$, $T \leq T_c$, at least to first order in ϵ . We then consider the consequences of our equation of state for polymer solutions and equilibrium polymerization of chains ($n = 0$). Section V contains a critical examination of several of the arguments adduced by Gujrati to argue that the equation of state for the $O(n)$ vector model is not analytic for $n < 1$. In Sec. VI we address arguments by Gujrati in his Sec. VI concerning the interchange of the limits $H \rightarrow 0$ and $V \rightarrow \infty$ and $n \rightarrow 0$ in the $O(n)$ vector model.

II. PARAMETRIC EQUATION OF STATE FOR THE n -VECTOR MODEL

The equation of state for the n -vector model contained in Eqs. (8.6)–(8.8) of Ref. 25 can be expressed in the expanded parametric form, correct to first order in $\epsilon = 4 - d$,

$$\begin{aligned} m &= m_0 r^\beta \theta, \\ h &= ar^{\beta\delta} \theta (1 - \theta^2), \\ \tau &= r \left\{ (2 - 3\theta^2) \right. \\ &\quad \left. + \epsilon (1 - \theta^2) \left[1 + \left[\frac{n-1}{n+8} \right] G(\theta^2) \right] + O(\epsilon^2) \right\}, \end{aligned} \quad (1)$$

where m is the magnetization per spin, $h = H/k_B T$ is the magnetic field divided by Boltzmann’s constant times the absolute temperature, and $\tau \equiv 1 - (T_c/T)$ measures the deviation of the temperature from its critical value and is positive for $T > T_c$. The singular function

$$G(\theta^2) \equiv \frac{[(1 - \theta^2)^{-\epsilon/2} - 1]}{\epsilon/2} = -\ln(1 - \theta^2) + O(\epsilon) \quad (2)$$

arises from Goldstone mode contributions. The critical exponents β and δ are the usual critical exponents, as in Ref. 25. With the choice of units for m and h such that

$$\begin{aligned} m_0 &= 1, \\ a &= 2 / \left\{ 1 + (\epsilon/2) \left[\frac{9}{n+8} \ln 3 - \ln 2 - 1 \right] + O(\epsilon^2) \right\}. \end{aligned} \quad (3)$$

The scaling variables

$$\begin{aligned} x &\equiv \tau / |m|^{1/\beta}, \\ y &\equiv h / |m|^\delta, \end{aligned} \quad (4)$$

satisfy Eqs. (8.6)–(8.9) of Ref. 25 to first order in ϵ , where we make the identification $w^2 = 1 - \theta^2$. Higher-order terms in Eqs. (8.6) of Ref. 25 simply contribute terms of higher order in ϵ to τ in Eq. (1) and to a in Eq. (3). It is straightforward to incorporate these higher-order terms into our equation of state. We have not done so here for simplicity, but consider the effects of one such term following Eq. (8) below. The parametric form in Eq. (1) is thus equivalent to the equation of state of Schäfer and Horner (SH). It is of a form similar to that first suggested by Schofield, Litster, and Ho,²⁶ and is somewhat more convenient than that of SH in that it is immediately apparent that the only singularities in the equation of state occur for $r = 0$ (the critical point) and $\theta^2 = 1$ (the coexistence curve). The scaling curve $|h| \sim (-\tau)^{\beta\delta}$ along which Gujrati asserts that there are anomalies in the equation of state corresponds to $0 < \theta^2 = \theta_1^2 < 1$, where θ_1 is a constant. The variables r, θ are alternative independent variables to τ, h in terms of which the equation of state $m(\tau, h)$ is expressed. One easily verifies that the Jacobian of the transformation, $\partial(\tau, h)/\partial(r, \theta)$ is nonvanishing for $r > 0$ to order ϵ for all values of ϵ, n, θ , of interest:

$$\begin{aligned} \frac{\partial(\tau, h)}{\partial(r, \theta)} &= ar^{\beta\delta} \left\{ 2 + \epsilon (1 - \theta^2) \left[1 + \left[\frac{n-1}{n+8} \right] G(\theta^2) \right] \right. \\ &\quad \left. + O(\epsilon^2) \right\}. \end{aligned} \quad (5)$$

Here and below, we require the ϵ expansion of the critical exponents to first order. These are well known²⁷

$$\alpha = \frac{\epsilon(4-n)}{2(n+8)} = \frac{\epsilon}{6} \left[1 - 4 \left[\frac{n-1}{n+8} \right] \right] + O(\epsilon^2),$$

$$\beta = \frac{1}{2} - \frac{3}{2(n+8)}\epsilon + O(\epsilon^2), \quad (6)$$

$$\beta\delta = \frac{3}{2} + \frac{\epsilon(n-1)}{2(n+8)} + O(\epsilon^2).$$

The nonvanishing of the Jacobian in Eq. (5) guarantees that τ and h uniquely determine r and θ . For a scaling equation of state such as Eq. (1) it implies, in particular, that $\tau/|h|^{1/\beta\delta}$ is a monotone function of θ which can therefore be solved for $\theta(\tau, h)$. Then Eq. (1) can be solved uniquely for $r(\tau, h)$ and thereby for $m(\tau, h)$. In fact, it is also easy to show that if Eq. (1) is truncated to order ϵ using the first of Eq. (2) for $G(\theta^2)$ and the exponents and coefficients $\beta, \beta\delta, a, m_0$ are evaluated to order ϵ for any fixed ϵ and n with $0 \leq \epsilon \leq 1$ and $n \geq 0$, then the exact (not ϵ expanded) Jacobian $\partial(\tau, h)/\partial(r, \theta)$ is strictly positive for all $r > 0$ and $0 < \theta^2 < 1$. This means that such a truncated equation can be used as a model equation of state, with $\epsilon=1$ and $n=0$ for example, and τ and h still uniquely determine r and θ . We note in passing that, to lowest (zeroth) order in ϵ , and with classical values for the exponents ($\beta = \frac{1}{2}, \delta = 3$), Eq. (1) reduces to the mean-field equation of state

$$h = \tau m + m^3. \quad (7)$$

The susceptibility, $\chi \equiv (\partial m / \partial h)_\tau$, can be evaluated by the method of Jacobians²⁸ and is readily found to be, to first order in ϵ ,

$$\chi = \left[\frac{m_0}{a} \right] r^{-\gamma} \left[1 + \frac{1}{2}\epsilon \left[\frac{n-1}{n+8} \right] \theta^2 G(\theta^2) + O(\epsilon^2) \right], \quad (8)$$

where $\gamma = \beta(\delta - 1)$ is the usual susceptibility exponent. According to Eq. (8), χ is nonnegative, to first order in ϵ , for $0 \leq \theta \leq 1$ when $n \geq 1$. It diverges as $\theta^2 \rightarrow 1$ for $n \neq 1$ because of the divergence of the Goldstone mode term $G(\theta^2)$. For $n < 1$, however, this term guarantees that $\chi(r, \theta)$ diverges to $-\infty$ as $\theta^2 \rightarrow 1$ and is negative for all $\theta^2 > \theta_0^2 = \text{const} < 1$. Thus, contrary to Gujrati's assertion, $m(\tau, h)$ is a decreasing function of h for all $\tau < 0$, for sufficiently small h , even though $m(\tau, h) \geq 0$ for all $h > 0$ and τ sufficiently small. This implies that x in Eq. (4) decreases from -1 on the coexistence curve and is more negative than -1 in the immediate vicinity of coexistence curve. This is dealt with in more detail in Sec. V below. While the susceptibility of the magnet is negative for $n < 1$, there is no corresponding violation of thermodynamic stability for the corresponding polymer solution—the physically relevant system. The relevant stability requirement is that $(h^2\chi + hm) \geq 0$, which is readily verified to be satisfied for all τ, h . The susceptibility in Eq. (8) is identical, to order ϵ , with that obtained from the correlation functions of Ref. 25 by setting the wave vector q equal to zero, as is to be expected.

A comment is in order concerning the status of an equation like Eq. (8). As an expansion in powers of ϵ it is obviously highly nonuniform in θ . For $\theta < 1$ it can be viewed as an expansion in the small parameter ϵ . As

$\theta \rightarrow 1$, however, it should be viewed as expressing the first term in an ϵ expansion for the coefficient of the singular function $G(\theta^2)$ that describes the divergence of χ on the coexistence curve for $n \neq 1$. When the term proportional to $G(\theta^2)$ in Eq. (8) is comparable to the first, care must be exercised in comparing them. For example, if one wishes to use Eq. (8) to find θ_0 , the value of θ at which χ vanishes, and thereby to find x_0 , the value of the scaling variable in x in Eq. (4) at θ_0 , one discovers that $x_0 + 1$ and $1 - \theta_0^2$ are determined only to within unknown constant factors. They can be determined to within factors of $1 + O(\epsilon)$ only if terms of order $\epsilon^2 G(\theta^2)$ in χ and $\epsilon^2(1 - \theta^2)G(\theta^2)$ in the equation of state are accounted for. These are available from Ref. 25 and easily incorporated. $G(\theta^2)$ in Eq. (1) must be multiplied by the factor

$$A = 1 + \frac{\epsilon}{n+8} \left[15 + \frac{n}{2} - \frac{30}{n+8} \right], \quad (9)$$

and in Eq. (8) by the factor

$$2\beta(1 - \epsilon/2)A = 1 + \frac{\epsilon}{n+8} \left[8 - \frac{30}{n+8} \right]. \quad (10)$$

[Eq. (9) follows from inspection of Eq. (8.7) of Ref. 25 for b_1 and Eq. (10) may be obtained either by differentiation or by inspection of Eqs. (8.4) and (8.5) of Ref. 25.] One then finds

$$x_0 \equiv x(\theta_0) = -1 - \epsilon \left[\frac{9}{n+8} \right] (1 - \theta_0^2) (< -1) \quad (11)$$

to within corrections of order $\epsilon^2(1 - \theta_0^2), (1 - \theta_0^2)^2$, etc., where

$$1 - \theta_0^2 = \left[\frac{1-n}{9} \right]^{2/\epsilon} \exp \left[\frac{2}{9} \left[8 - \frac{30}{n+8} \right] + O(\epsilon) \right]. \quad (12)$$

Note that x_0 in Eq. (11) does not depend upon the value of A , but only upon keeping terms of $O(\epsilon)$ in $2\beta(1 - \epsilon/2)$, whereas $1 - \theta_0^2$ in Eq. (12) requires $O(\epsilon)$ terms in A even to order ϵ^0 . It should not be surprising that terms of $O(\epsilon^2)$ in the coefficient of $G(\theta^2)$ are required at θ_0 since $\epsilon G(\theta^2)$ is itself of order unity there. This is not a pathology of $n < 1$; rather, it is a feature of the crossover between two kinds of singular behavior encountered in the n -vector model whenever $n \neq 1$. This was noted earlier by Wallace and Zia²⁹ in connection with the $n > 1$ vector model. In particular, our Eq. (12) is equivalent to Eq. (3.71) of Ref. 29(b) for the value of y_0 at which the two dominant terms in χ become equal when $n > 1$. For $\theta > \theta_0$, the susceptibility is negative and $x \leq -1$. For $\theta < \theta_0$, the susceptibility is positive.

Similar care must be exercised in using Lawrie's equation of state to evaluate y_0 , the value of y at which $\chi = 0$ or y^* at which x returns to -1 . Because Lawrie's equation of state is correct only to order ϵ^1 , the value of y_0 and y^* obtained from it are reliable only to within unknown constant factors. This applies to the value of y^* quoted in Ref. 16 in the equation following Eq. (32). The value of y^* can be obtained to within a factor $1 + O(\epsilon)$ by using

Eq. (9) with Eq. (1) and is found to be $y^* = y_0 \exp[1 + O(\epsilon)] > y_0$, where $y_0 = 2(1 - \theta_0^2)$ with $(1 - \theta_0^2)$ given by Eq. (12).

It should be noted that if the logarithmic form of $G(\theta^2)$ in Eq. (2) were used in the ϵ expansion, then terms of order $\epsilon^n \ln^n(1 - \theta^2)$ would appear in the ϵ expansion of χ , and there would be no hope of making a sensible analysis for $\theta \rightarrow 1$. If these terms are summed into the exponentiated form of $G(\theta^2)$ given first in Eq. (2) then the higher-order terms in ϵ in Eq. (8) take the form of an ϵ expansion for the coefficient of $G(\theta^2)$ and for the constant term plus *less singular* functions of θ that, for small ϵ , vanish as $\theta^2 \rightarrow 1$. A systematic treatment is then possible even for θ approaching unity. The equation of state of Schäfer and Horner incorporates the behavior near the coexistence curve pointed out by Wallace and Zia²⁹ into a convenient functional form that holds throughout the h - T plane near the critical point. The relationship between the $\chi=0$ locus found here and that found at large field in the mean-field equation of state⁸ and by exact arguments is discussed in Sec. VII.

III. FREE ENERGY

The parametric equation of state in Eq. (1) can be integrated to yield a thermodynamic potential

$$f(\tau, h) = \frac{1}{2} am_0 r^{\beta(\delta+1)} [\hat{F}_0(\theta) + \epsilon \hat{F}_1(\theta) + O(\epsilon^2)] \quad (13)$$

from which the magnetization m and the energy

$$e \equiv - \frac{J}{k_B T_c} N^{-1} \left\langle \sum_{\langle i, j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j \right\rangle$$

can be obtained by differentiation:

$$m = \left[\frac{\partial f}{\partial h} \right]_{\tau}, \quad (14)$$

$$e = \left[\frac{\partial f}{\partial \tau} \right]_h. \quad (15)$$

Combining Eqs. (1), (13), and (14) and using Jacobians to express the derivatives in terms of r and θ , one obtains the following differential equations for $\hat{F}_0(\theta)$ and $\hat{F}_1(\theta)$

$$\hat{T}_0 \hat{F}'_0(\theta) - 2\hat{T}'_0(\theta) \hat{F}_0(\theta) = 4\theta, \quad (16)$$

$$\begin{aligned} & \hat{T}_0 \hat{F}'_1(\theta) - 2\hat{T}'_0(\theta) \hat{F}_1(\theta) \\ &= \hat{F}_0 \left[-\frac{\alpha}{\epsilon} \hat{T}'_0 + 2\hat{T}'_1 \right] \\ &+ \theta \hat{H} \left[-2\hat{T}'_0(\theta) \left[\frac{\beta\delta - 3/2}{\epsilon} \right] - 3\hat{T}'_1 \right] \\ &+ \hat{T}_1 [2\theta \hat{H}'(\theta) - \hat{F}'_0], \end{aligned} \quad (17)$$

where $\hat{T}_0 = 2 - 3\theta^2$,

$$\hat{T}_1 = (1 - \theta^2) \left[1 + \left[\frac{n-1}{n+8} \right] G(\theta^2) \right],$$

and $\hat{H}(\theta) = \theta(1 - \theta^2)$, and where primes denote the first derivative with respect to θ . We have made use of the exponent scaling law $\beta(\delta+1) = 2 - \alpha$ and of the known limiting behavior of the exponents with ϵ given in Eq. (6). Equation (16) has the general solution

$$\hat{F}_0(\theta) = \theta^2(1 - \frac{3}{4}\theta^2) + \frac{1}{4}a_0(2 - 3\theta^2)^2. \quad (18)$$

The coefficient a_0 is arbitrary in the solution of Eq. (16), but is determined by the requirement that $\hat{F}_1(\theta)$ be nonsingular at $\theta^2 = \frac{2}{3}$. It is found to be

$$a_0 = n/(4-n). \quad (19)$$

Thus, for $n \rightarrow 0$ the scaling part of the free energy $\hat{F}_0(\theta) \equiv \theta^2(1 - \frac{3}{4}\theta^2)$ vanishes identically for $H \rightarrow 0$, $T > T_c$ (i.e., for $\theta \rightarrow 0$), as does the total free energy, in accord with the requirement that the osmotic pressure of the corresponding polymer solution vanish with vanishing activity of polymers.

Using Eq. (6), the solution of Eq. (17) for $\hat{F}_1(\theta)$ is found to be

$$\begin{aligned} \hat{F}_1(\theta) &= \frac{1}{4}a_1(2 - 3\theta^2)^2 + \frac{n^2 + 18n + 8}{4(4-n)(n+8)}\theta^2 \\ &- \frac{5n^2 + 104n + 80}{16(4-n)(n+8)}\theta^4 \\ &+ \frac{(n-1)(n+4)}{2(4-n)(n+8)} \left[1 - \left[\frac{n+8}{n+4} \right] \theta^2 \right] \\ &\times (1 - \theta^2)G(\theta^2). \end{aligned} \quad (20)$$

To determine the arbitrary coefficient a_1 would require knowing the equation of state of Eq. (1) to second order in ϵ . Then the requirement that $\hat{F}_2(\theta)$, the second order in ϵ contribution to $\hat{F}(\theta)$, be nonsingular at $\theta^2 = \frac{2}{3}$ would determine a_1 . We discuss this further below.

The energy e and constant-field heat capacity c_h corresponding to (20) can be obtained by differentiation using Jacobians and are found to be³⁰

$$e = \left[\frac{\partial f}{\partial \tau} \right]_h = \frac{1}{2} am_0 r^{1-\alpha} (\hat{E}_0 + \epsilon \hat{E}_1), \quad (21)$$

$$c_h = \left[\frac{\partial e}{\partial \tau} \right]_h = \frac{1}{2} am_0 r^{-\alpha} (\hat{C}_0 + \epsilon \hat{C}_1), \quad (22)$$

where

$$\hat{E}_0 = \frac{n}{4-n} (1 - \frac{3}{2}\theta^2) - \theta^2/2, \quad (23)$$

$$\begin{aligned} \hat{E}_1 &= a_1 (1 - \frac{3}{2}\theta^2) - \frac{n(n+20)}{4(4-n)(n+8)} + \frac{3n^2 + 68n + 64}{8(n+8)(4-n)}\theta^2 \\ &+ \frac{2(n-1)}{(n+8)(4-n)} (1 - \theta^2)G(\theta^2), \end{aligned} \quad (24)$$

and

$$\hat{C}_0 = \frac{n}{2(4-n)} + \frac{1}{2}\theta^2, \quad (25)$$

$$\hat{C}_1 = \frac{1}{2}a_1 - \left[\frac{n(n+44)}{8(4-n)(n+8)} \right] - \left[\frac{3}{n+8} \right] \theta^2 + \frac{n-1}{4(n+8)}(1-\theta^2)^2 G(\theta^2), \quad (26)$$

and where we have used the scaling relation $\beta(\delta+1)=2-\alpha$. Alternatively, they may be found through the generalized Euler relations implied by the homogeneity of f :

$$(2-\alpha)f = \tau e + \beta\delta mh, \quad (27)$$

$$(1-\alpha)e = \tau c_h + \beta\delta \left[\frac{\partial m}{\partial \tau} \right]_h, \quad (28)$$

where we have made use of the Maxwell relation

$$\left[\frac{\partial e}{\partial h} \right]_\tau = \left[\frac{\partial m}{\partial \tau} \right]_h. \quad (29)$$

It is relatively easy to verify that (18)–(26) satisfy (27)–(29) to order ϵ as identities in r and θ .

By examining the requirement of analyticity of $\hat{F}_2(\theta)$ at $\theta^2 = \frac{2}{3}$ it is possible to show that a_1 must be of the form $a'_1(n)/(4-n)^2$, where $a'_1(n=4)=16$. This much can be deduced without detailed knowledge of the second-order-in- ϵ contribution to the equation of state. The full dependence of a_1 upon n can be determined from the heat-capacity amplitude ratio A^+/A^- calculated by Brezin, LeGuillou, and Zinn-Justin.³¹ This requires a_1 to be

$$a_1 = \frac{n(208-n^2)}{4(4-n)^2(n+8)}. \quad (30)$$

With this value of a_1 we also reproduce Aharony and Hohenberg's³² scaled amplitude

$$\bar{A} = \frac{1}{2}am_0[\hat{T}_0(0)]^\alpha \alpha[\hat{C}_0(0) + \epsilon\hat{C}_1(0)].$$

This independent check on a_1 gives us considerable confidence in both a_1 itself and our thermodynamic potential as a whole.³³

We remark that the factors $(4-n)$ in the denominators of a_0 and $\hat{F}_1(\theta)$ are essentially the critical exponent α to lowest order in ϵ [cf. Eq. (6)] and arise because the free energy has logarithmic singularities when $\alpha=0$. One could perhaps improve the equation of state by replacing $4-n$ by $2(n+8)\alpha/\epsilon$ in Eqs. (19), (20), and (30) and appropriately modifying higher-order terms, but as this is not a problem for $n \leq 1$ we have not done so here.

IV. THE $n \rightarrow 0$ LIMIT, EQUILIBRIUM POLYMERIZATION, AND POLYMER SOLUTIONS

As noted above, there is an exact correspondence between the $n \rightarrow 0$ limit of the $O(n)$ vector model on a lattice and a model for equilibrium polymerization^{7,8} of chains from monomers. The partition function for this model of polymerization can be written as

$$Y = \sum_{N_p} \sum_{N_b} \sum_{N_1} (2K_1)^{N_p} (K'_p)^{N_b} \left(\frac{1}{2}\right)^{N_1} \Gamma(N_p, N_b, N_1; N), \quad (31)$$

where K_1 is the equilibrium constant for activation of a monomer (statistical weight of an activated monomer relative to normal, unactivated monomer), K'_p is the equilibrium constant for a chain polymer of length m in a given configuration of cells to propagate to a chain of length $m+1$ by adding an unactivated monomer in a specified cell adjacent to either end, N_p is the total number of polymers (including "one-cell polymers," i.e., activated monomers), N_b is the total number of bonds between monomers, N_1 is the number of "one-cell polymers," and $\Gamma(N_p, N_b, N_1; N)$ is the number of ways of arranging N_p polymers containing N_b bonds, N_1 of which are "one-cell polymers" on a lattice of N sites such that no cell is visited by more than one polymer (excluded volume). We have shown⁸ that this partition function is identical to that of the $n \rightarrow 0$ vector model with the identification of variables given below, and moreover, that in the mean-field approximation to the $n \rightarrow 0$ vector model it becomes identical to the well-known Tobolsky-Eisenberg³⁴ theory of equilibrium polymerization. A somewhat different mapping between polymer solutions and the lattice $n \rightarrow 0$ vector model has been given by Gujrati⁵ in which the activity of a polymer end is denoted by η and that for a bond by κ and only polymers with at least one bond (two monomers in our description) are allowed. While these mappings are quite different in some regions of the parameter space (for example, our mapping is 1-1 throughout the positive H half of the H - T plane for the magnet while Gujrati's is not), they become identical in the scaling limit $H \rightarrow 0$, $T \rightarrow T_c$, where the number concentration and volume fraction of polymers both vanish, and the mean molecular weight diverges. In this limit, neglecting corrections to scaling, both models can be described by the identifications,

$$(2K_1)^{1/2} = \eta = h,$$

$$K'_p = \kappa = \tilde{J} = J/k_B T,$$

$$\frac{\Pi v_0}{k_B T} = f \equiv N^{-1} \ln Z, \quad (32)$$

$$\phi_{ch} = \phi_l = \tilde{J} \left[\frac{\partial f}{\partial \tilde{J}} \right] = -e,$$

$$x_p = \phi_p = h^2 \left[\frac{\partial f}{\partial h^2} \right]_{\tilde{J}} = \frac{1}{2} hm,$$

where Π is the osmotic pressure of the polymer solution, v_0 the volume of a lattice cell, Z the partition function for the lattice magnet, J the coupling constant between spins, ϕ_{ch} the volume fraction for monomers in polymers (i.e., the fraction of cells in which the monomers are in a polymer), and x_p is the number concentration of polymers multiplied by v_0 (i.e., the number of polymers divided by the number of cells). The quantities ϕ_l and ϕ_p are analogous variables in Gujrati's⁵ correspondence to ϕ_{ch} and x_p . The mean number of monomers in a polymer is given by $\bar{N} = \phi_{ch}/x_p$. Taking the limit $n \rightarrow 0$ in our equation of state above, we obtain for equilibrium polymerization and polymer solutions,

$$\begin{aligned}
h &= ar^{\beta\delta}\theta(1-\theta^2), \\
\tau &= r\{2-3\theta^2+\epsilon(1-\theta^2)[1-\frac{1}{8}G(\theta^2)]+O(\epsilon^2)\}, \\
\frac{\Pi v_0}{k_B T} &= \frac{1}{2}am_0r^{2-\alpha}\left\{\theta^2(1-\frac{3}{4}\theta^2)+\frac{\epsilon}{16}[\theta^2-\frac{5}{2}\theta^4\right. \\
&\quad \left.-(1-2\theta^2)(1-\theta^2)G(\theta^2)]+O(\epsilon^2)\right\}, \\
x_p &= \frac{1}{2}am_0r^{2-\alpha}\theta^2(1-\theta^2), \\
\phi_{ch} &= \frac{1}{4}am_0r^{1-\alpha}\left\{\theta^2-\frac{\epsilon}{2}[\theta^2-\frac{1}{4}(1-\theta^2)G(\theta^2)]+O(\epsilon^2)\right\}, \\
\bar{N} &= [2r(1-\theta^2)]^{-1}\left\{1-\frac{\epsilon}{2}\left[1-\frac{1}{4}\frac{(1-\theta^2)G(\theta^2)}{\theta^2}\right]\right. \\
&\quad \left.+O(\epsilon^2)\right\}.
\end{aligned} \tag{33}$$

Our results for the osmotic pressure Π above is in agreement with that of Knoll, Schäfer, and Witten.⁴ Combining their Eqs. (1.1) and (4.15) with the identification that their w is equal to $1-\theta^2$ in our notation and that their c_p is our x_p divided by v_0 , leads to our $\Pi v_0/k_B T$.³³ The first order in ϵ term in \bar{N} above is well behaved for $0 \leq \theta^2 \leq 1$ since $G(\theta^2) \sim \theta^2$ near $\theta=0$.

In the dilute ($\theta \rightarrow 0$) limit x_p , ϕ_{ch} , and Π all vanish proportionally to θ^2 (that is, to K_1), as expected, and $\bar{N} \propto r^{-1}$. These results are all in accord with the Tobolsky-Eisenberg (TE) theory³⁴ of polymerization. In the semidilute ($\theta \rightarrow 1$) limit, x_p vanishes proportionally to $K_1^{1/2}$ while \bar{N} diverges proportionally to $K_1^{-1/2}$ and ϕ_{ch} remains nonzero and finite and varies as $r^{1-\alpha} \sim (-\tau)^{1-\alpha}$. These are again consistent with the TE theory except for the prediction that $\alpha > 0$, a nonclassical critical effect. The Des Cloizeaux scaling law,² that $\Pi v_0/k_B T x_p$ is a function of the single variable $x_p \bar{N}^{d\nu}$ amounts to the observation that, with the scaling law $d\nu = 2 - \alpha$, each of these quantities is a function only of θ , not of r , and therefore each is a function of only the other, not of any additional variables. In the dilute limit we obtain the result

$$\frac{\Pi v_0}{k_B T x_p} = 1 + b x_p \bar{N}^{d\nu} + \dots, \tag{34}$$

where b is a numerical constant. This has the physical content that the effective excluded volume between the polymers is given by their radius of gyration, $\bar{N}^{d\nu}$. In the semidilute limit we recover the famous Des Cloizeaux limiting law²

$$\frac{\Pi v_0}{k_B T} = A \phi_{ch}^{d\nu/(d\nu-1)} \quad (d\nu = 2 - \alpha), \tag{35}$$

where A is a constant, by examining the powers of r in

$\Pi v_0/k_B T$ and ϕ_{ch} and noting that the corresponding functions of θ remain positive as $\theta \rightarrow 1$.

The radius of gyration of the polymer chains is conveniently measured by their end-end correlation length R , which is, in turn, given by the transverse correlation length² of the $O(n)$ vector model in the limit $n \rightarrow 0$. This is found to be²⁵ (with R measured in lattice spacings)

$$R \sim r^{-\nu}(1-\theta^2)^{-1/2}. \tag{36}$$

This has an interesting physical interpretation in terms of the "blob" picture of the semidilute limit. First note that for $\theta < 1$, and $r \rightarrow 0$, this is consistent with swollen polymers in the dilute limit where $R \sim \bar{N}^\nu$. However, as $\theta \rightarrow 1$ these formulas become inconsistent. Instead, for fixed r and $\theta \rightarrow 1$, we have $R \sim \bar{N}^{1/2}$, the random walk result, but with a coefficient that varies as $r^{-(\nu-1/2)}$. A crude scaling argument due to De Gennes¹⁵ sheds light on this result. If we take $r^{-\nu}$ as the distance scale on which a polymer chain remains swollen before losing correlations with itself due to encounters with monomers on other chains, then there should be $M \sim r^{-1}$ monomers from this polymer in this "blob" and $B = NM^{-1}$ such blobs, each of radius M^ν , and these blobs will execute a random walk with final end to end distance

$$R \sim M^\nu B^{1/2} \sim r^{-(\nu-1/2)} \bar{N}^{1/2}. \tag{37}$$

We remark that r^ν is essentially the momentum cutoff κ of Ref. 4 [cf. Eq. (2.33)] and essentially the mass m of Sec. 10 of Ref. 25. The identification of $r^{-\nu}$ as the distance scale on which a polymer is swollen is in accord with the behavior of the energy-energy correlation function of the $O(n)$ vector model, which corresponds to the monomer-in-a-polymer, monomer-in-a-polymer correlation function for the polymer solution. This correlation function drops off more rapidly for distance x greater than $r^{-\nu}$ than for $x < r^{-\nu}$ (although not necessarily exponentially³⁵), so that $r^{-\nu}$ can be identified as the distance scale (in units of the lattice spacing) on which a polymer ceases to distinguish itself from other polymers.

Although the concentration of chains, x_p , vanishes as $h \rightarrow 0$ in the polymerized phase (semidilute limit) it should not be thought that the system consists of few polymers or a single polymer. Indeed the number of other polymers which are expected to be found within the radius of gyration of any single polymer is given by

$$R^d x_p = \frac{\frac{1}{2} am_0 \theta^2}{(1-\theta^2)^{d/2-1}} \tag{38}$$

independently of r . This number vanishes as $\theta \rightarrow 0$ as is to be expected when the separation between polymers is much greater than their size. In the semidilute ($\theta \rightarrow 1$) limit, however, this diverges proportionally to $h^{-(d-2)/2}$. Thus every polymer chain is penetrated by an infinite number of other chains in the limit $h \rightarrow 0$ whenever $d > 2$. This conclusion is in complete accord with the conventional picture of strongly interpenetrating polymers which screen each other according to the De Gennes "blob" picture, but is in stark contrast to Gujrati's assertion¹⁷ that the state as $h \rightarrow 0$ for $T < T_c$ consists of a single polymer chain.

As remarked above, the negative magnetic susceptibility of the (nonexistent) $n=0$ magnet does *not* imply any thermodynamic instability for the corresponding polymer solution. The criteria for thermodynamic stability of the polymer system are

$$\begin{aligned} \left[\frac{\partial x_p}{\partial \ln K_1} \right]_{K'_p} \geq 0, \quad \left[\frac{\partial \phi_{ch}}{\partial \ln K'_p} \right]_{K_1} \geq 0, \\ \left[\frac{\partial x_p}{\partial \ln K_1} \right]_{K'_p} \left[\frac{\partial \phi_{ch}}{\partial \ln K'_p} \right]_{K_1} - \left[\frac{\partial x_p}{\partial \ln K'_p} \right]_{K_1} \left[\frac{\partial \phi_{ch}}{\partial \ln K_1} \right]_{K'_p} \geq 0. \end{aligned} \quad (39)$$

In terms of the magnetic variables, these become (neglecting correction-to-scaling terms)

$$\begin{aligned} \frac{1}{4}(hm + h^2\chi) \geq 0, \quad c_h \geq 0, \\ \frac{1}{4} \left[(hm + h^2\chi)c_h - h^2 \left[\frac{\partial m}{\partial \tau} \right] h^2 \right] \geq 0. \end{aligned} \quad (40)$$

It is straightforward to verify that these inequalities are satisfied, to first order in ϵ , for $0 \leq \epsilon \leq 1$, $0 \leq n < 4$, $0 \leq \theta \leq 1$. For $n=0$ they become, in the scaling variables,

$$\begin{aligned} \frac{1}{4} am_0 r^{2-\alpha} \theta^2 (1-\theta^2) \left[2 - \theta^2 - \frac{\epsilon}{16} \theta^2 (1-\theta^2) G(\theta^2) + O(\epsilon^2) \right] \geq 0, \\ \frac{1}{4} am_0 r^{-\alpha} \{ \theta^2 - \epsilon [\frac{3}{4} \theta^2 + \frac{1}{16} (1-\theta^2)^2 G(\theta^2)] + O(\epsilon^2) \} \geq 0, \\ \frac{1}{16} (am_0 r^{1-\alpha})^2 \theta^2 (1-\theta^2) \{ \theta^2 - \epsilon [\frac{3}{4} \theta^2 + \frac{1}{16} (1-\theta^2)(2-\theta^2) G(\theta^2)] + O(\epsilon^2) \} \geq 0. \end{aligned} \quad (41)$$

Thus, the polymer system is thermodynamically stable against all possible fluctuations in number and length of polymers near the critical point for all accessible values of its parameters.

The negative susceptibility of the magnet has a physical interpretation in the polymer language as ‘‘correlation hole’’ effect. The second derivative of $f = N^{-1} \ln Z$ with respect to $\ln(h)$ (the chemical potential of a polymer end) gives $hm + h^2\chi$. According to very general statistical-mechanical arguments,³⁶ this can be written as the integral over all space of the (cumulant) average of the density of polymer ends at position \mathbf{x} times that density at the origin. The term hm may be identified as the integral over a Dirac δ function giving the correlation of an end with itself, while the term $h^2\chi$ may be identified as the integral over the correlation function of one end at the origin with *other* ends at position \mathbf{x} . In the dilute limit ($\theta \rightarrow 0$), when polymers are widely separated compared to their spatial extent, the presence of a polymer end at the origin guarantees the presence of another polymer end (the other end of the same polymer) nearby, and therefore an enhancement over the mean of the density of other ends, so that $h^2\chi \geq 0$. In the semidilute limit ($\theta \rightarrow 1$), however, the presence of a polymer end at the origin guarantees the presence of a (long) polymer near the origin and the excluded volume of that polymer implies a decrease (below the mean) of the density of other ends nearby, thus leading to a negative value of $h^2\chi$. Thus it is to be expected that χ is positive for small θ and becomes negative as $\theta \rightarrow 1$.

This difference between the behavior near $\theta=0$ (pairs of ends moving together) and near $\theta=1$ (‘‘dissociated’’ ends moving more or less independently) is also the source of the fundamental difference in the dependence of con-

centration of chain polymers, $x_p = \frac{1}{2}hm$, in the limit $n \rightarrow 0$ upon the activity for a polymer end, h . As $\theta \rightarrow 0$ the polymers move as distinct units so that the ends are tied together and $x_p \sim h^2$. As $\theta \rightarrow 1$, the polymer ends are effectively ‘‘dissociated’’ and $x_p \sim (h^2)^{1/2} \sim h$, a result characteristic of a dissociation equilibrium. This point has been discussed in more detail in Ref. 11 in the context of simple equilibrium theories of polymerization. The divergent, negative susceptibility implies that x_p deviates from its asymptotic $\theta^2 \approx 1$ behavior as $x_p \sim \frac{1}{2}m_0(T)h - \Gamma_0(T)h^{d/2}$, where $m_0(T)$ is the spontaneous magnetization and $\Gamma_0(T)$ is a positive function of T . This is the result of the ‘‘correlation hole’’ effect. Note that while x_p exhibits ‘‘negative deviations’’ from its limiting behavior, these are *not* strong enough to violate the required monotonicity of x_p in h (stability).

Two additional remarks are warranted. First, the ratio $(h^2\chi)/(hm)$ tends to zero as $\theta \rightarrow 1$ for $2 < d \leq 4$. Since hm is the (unbiased) probability density for an end to be at the origin, this ratio is the difference between the total number of (other) polymer ends anywhere in the space *given* that a polymer end is fixed and the total number of other polymer ends *independent* of whether there is a polymer at the origin or not. That this quantity vanishes as $\theta \rightarrow 1$ shows that the correlation hole effect, while present, is really a rather weak effect involving subtle cancellations. Second, in the compressibility relation³⁶ for fluids,

$$\left[\frac{\partial \rho}{\partial (\mu/k_B T)} \right]_T = \rho^2 k_B T K_T = \rho + \rho^2 \int d\mathbf{x} h(\mathbf{x}), \quad (42)$$

the first term plays a role analogous to hm , above, while the second plays a role analogous to $h^2\chi$. In liquids it is

virtually always the case that the second term is negative, and moreover comparable in magnitude to the first. Thus the negative value for $h^2\chi$ for $n=0$, i.e., in polymer solutions, is not to be thought of as unusual, and the fact that it vanishes compared to hm indicates that even in the semidilute limit where the polymers are strongly interpenetrating they are nevertheless (relatively) weakly interacting when compared with normal molecules in a liquid.

Equation (33), to lowest order in ϵ , is very similar to the equation of state we proposed earlier⁷ on an *ad hoc* basis to describe equilibrium polymerization using the $n \rightarrow 0$ vector model. Equation (33) with $\epsilon=0$ differs in one important respect from Eq. (7) of Ref. 7. To lowest order in ϵ , Eq. (33) implies that the parameter b^2 of Ref. 7 is $\frac{3}{2}$ rather than 2, the value deduced there. The value $b^2=2$ would be correct if the simple ($\epsilon=0$) scaling form proposed there held for nonclassical ($\epsilon>0$) values of the exponents. If, however, τ and ϕ_c contain corrections of order ϵ [which they do according to Eq. (33)], then the value of b^2 deduced from the Maxwell relation in Eq. (29) above depends upon these corrections as well as upon the ϵ dependence of α and $\delta-3$, and the resulting value of b^2 is $\frac{3}{2}$ rather than 2.

V. RELATION TO GUJRATI'S WORK

In this section we address several specific arguments used by Gujrati to argue that the $O(n)$ vector model is not analytic for $h > 0$ when $n < 1$. First we show that there is no difficulty with finding solutions to Lawrie's equation of state as x can in fact be less than -1 . Next we show that the divergence of various renormalized magnetic coupling constants is expected when $\chi=0$ and that this is not an intrinsic problem with the equation of state as a function of h . Finally we discuss the equivalence of polymers to two different n -component magnetic models, one of which has $O(n)$ symmetry, and the other of which has n -hypercubic symmetry.

Gujrati's contention that Lawrie's²⁴ equation of state is inconsistent with a real solution for $m(H, T)$ when $n < 1$ is based on his (erroneous) conclusion that $m(H, T)$ must be an increasing function of H at $H=0$ for T sufficiently close to T_c . Unfortunately Gujrati's Eq. (32) contains two typographical errors that make the argument after it difficult to follow. Lawrie's equation of state in Gujrati's form should read

$$(3+x)^{\epsilon/2} \left[1+x \left(\frac{2}{3+x} \right)^{3\epsilon/(n+8)} \right] = 9y \left[1 + \left(\frac{n-1}{9} \right) \left(\frac{3+x}{y} \right)^{\epsilon/2} \right] / (n+8) \quad (43)$$

with x and y given by Eq. (4). As $H \rightarrow 0$, with $T < T_c$, $x \rightarrow -1$, and $y \rightarrow 0$. If, as contended by Gujrati, x must be greater than -1 for $n < 1$, then the left-hand side of Eq. (43) would indeed remain positive and the right-hand side become negative sufficiently close to $H=0$. However, this is neither required, nor in fact the case. Gujrati argues, following his Eq. (32), that, given that

- (a) $m(\tau, h) > 0$ for $h > 0$,
- (b) $m(\tau, h \rightarrow 0^+) > 0$ for $\tau < 0$,
- (c) $m(\tau, h=0) = 0$ for $\tau \geq 0$,
- (d) $m(\tau, h)$ smooth,

then $m(\tau, h)$ must be an increasing function of h for $h=0$ and τ sufficiently small. This would then imply that $x > -1$. However, inspection of Eqs. (1), (3), and (4) shows that they satisfy conditions (a)–(d) above and that

$$x = \frac{(2-3\theta^2) + \epsilon(1-\theta^2) \left[1 + \left(\frac{n-1}{n+8} \right) G(\theta^2) \right]}{\theta^{1/\beta}} = -1 + \epsilon \left(\frac{n-1}{n+8} \right) (1 + \theta^2) G(\theta^2) + O(1-\theta^2), \quad (44)$$

and is therefore *less* than -1 for θ^2 sufficiently close to 1 whenever $n < 1$. Thus these equations constitute a counterexample to Gujrati's argument, which is therefore in error, and thus the left-hand side of Eq. (43) as well as the right-hand side may become negative for h sufficiently small and $\tau < 0$, so that no contradiction occurs.

The fatal error in Gujrati's argument following his Eq. (32) is his conclusion that because $m(h, T)$ must be positive for positive h , and because the spontaneous magnetization approaches zero as $T \rightarrow T_c$, therefore the initial slope of m versus h must be positive. In fact, it can be infinitely negative and is so for the equation of state in Eqs. (1)–(4). The magnetization m decreases with increasing h , passing through a minimum at $h=h_0(\tau)$ where $h_0(\tau) \sim (-\tau)^{\beta\delta}$. Thus the distance to the minimum and the consequent depth of the minimum decrease as $T \rightarrow T_c$ in such a way that the minimum value of m remains positive. It is relatively easy to construct simple model functions $m(h, \tau)$ which illustrate this possibility and therefore also serve as counterexamples to Gujrati's conclusion. For example, the function (defined for $h \geq 0$, $\tau \leq 0$)

$$m(h, \tau) = |\tau|^{1/2} - h^{1/4} |\tau|^{1/4} + h^{1/2} \quad (45)$$

satisfies conditions (a)–(c) above and has the properties

- (i) $m(0, \tau) = |\tau|^{1/2} \rightarrow 0$ as $\tau \rightarrow 0^-$,
- (ii) $(\partial m / \partial h)_{\tau \rightarrow 0} \rightarrow -\infty$ as $h \rightarrow 0$ for all $\tau < 0$. This simple example does not, of course, satisfy condition (d) for $\tau=0$, $h > 0$ or for $\tau > 0$. The slightly more complicated example

$$m(h, \tau) = h \left[\frac{(h^2 + \tau^2)^{1/2} - \tau}{h^2} \right]^{1/2} \times \left[2 - \left[1 + \frac{\tau}{(h^2 + \tau^2)^{1/2}} \right]^{1/4} \right] \quad (46)$$

satisfies (a)–(d) and has the properties

- (1) $m(h, \tau)$ analytic for all real h , except on $h=0$, $\tau \leq 0$,
- (2) $m(0^+, \tau) = 2^{3/2} |\tau|^{1/2}$ ($\tau < 0$),
- (3) $m(h, \tau) \sim h\tau^{-1/2}$, $\tau > 0$, $h^2 \ll \tau^2$
- (4) $\lim_{h \rightarrow 0} (\partial m / \partial h)_{\tau} = -\infty$ for all $\tau < 0$.

It also satisfies scaling with the (unphysical) exponents $\alpha=\beta=\gamma=\delta^{-1}=\frac{1}{2}$. For more realistic exponents it is easiest to turn to a parametric equation of state such as the one we have employed. We have given these simple examples to emphasize the point that, although plausible sounding, Gujrati's conclusion is demonstrably false.

In his Secs. III, IV, and VII Gujrati argues that the divergence of a (renormalized) coupling constant in his field theoretic calculation precludes analytic continuation of the equation of state beyond this divergence. This is a legitimate concern if the equation of state is expressed as a perturbation series in this coupling constant. Schäfer and Horner do not do this. The (zero momentum) coupling constants are derivatives of a free energy, $\Gamma(t, m)$ viewed as a function of m , with respect to components of the magnetization [cf. Eq. (25) of Ref. 25 and Eq. (5) of Ref. 16]. The vanishing of χ implies that m passes through an extremum as a function of h , which in turn implies that Γ and its derivatives will, in general, be double-valued functions of m with singularities at the locus $\chi=0$ as functions of m . This does not imply, however, that the free energy $f(t, h) = \Sigma h^\alpha m^\alpha - \Gamma(t, m)$ as a function of the field or any of its derivatives is singular as a function of h on the locus $\chi=0$, and in fact they are not for the n -vector model with $n < 1$. Schäfer and Horner express the coupling constants (which are indeed divergent for $n < 1$ at $\chi=0$) in terms of smoothly varying nondivergent quantities [cf. their Eqs. (8.1) and (8.2)] which, in turn, determine the equation of state in a manner which is nonsingular even when $\chi=0$.

A particularly simple and relevant example illustrates the possibility of analytic continuation through the locus of diverging coupling constants. In the limit $J \rightarrow 0$ the $n \rightarrow 0$ vector model on a lattice with fixed length spins is exactly soluble,⁸ with partition function

$$Z = (1 + \frac{1}{2}h^2)^N. \quad (47)$$

From this we readily deduce that

$$\begin{aligned} m^{(\alpha)} &= h^{(\alpha)}(1 + \frac{1}{2}h^2)^{-1}, \\ h^{(\alpha)} &= m^{(\alpha)}m^{-2}[1 \pm (1 - 2m^2)^{1/2}], \\ \chi &= (1 - \frac{1}{2}h^2)(1 + \frac{1}{2}h^2)^{-2}. \end{aligned} \quad (48)$$

Note that $\chi \rightarrow 0$ when $h^2 \rightarrow 2$ or ∞ and that h is a double-valued function of m with a singular point at $m^2 = \frac{1}{2}$, but that m is analytic in h for all real h . The coupling constants are readily calculated as derivatives of h^α with respect to components of m . One obtains, for example, in the notation of Schäfer and Horner, the Ward identities

$$\begin{aligned} \Gamma_{l,n}^{(3)}(0,0,0) &= (m\chi)^{-1} - hm^{-1}, \\ \Gamma_{uu't}^{(4)}(0,0,0,0) &= -hm^{-3} + m^{-2}\chi^{-1}. \end{aligned} \quad (49)$$

These formulas are quite general and can be derived using only the rotational invariance of Γ , but are easily checked directly in this simple case. It is clear that these coupling constants (and many others) will diverge when $\chi=0$, both for the exactly solved $O(n)$ vector model at $J=0$, and for the ϵ expansion of the equation of state given above. This

is a simple consequence of $\chi=0$ and is to be expected everywhere along the locus $\chi=0$. For the $J=0$ limit it is simple to show that Gujrati's coupling constants have the behavior near $\chi=0$,

$$\begin{aligned} \lambda_T &\equiv \frac{1}{3}\Gamma_{uu't} \sim \chi^{-1}, \\ \lambda_{TL} &\sim \chi^{-3}, \\ \lambda_L &\sim \chi^{-5}, \end{aligned} \quad (50)$$

and this is to be expected quite generally along the locus $\chi=0$ provided only that $(\partial^2 m / \partial h^2)_\tau$ does not vanish there. [We note in passing that the coupling constants in Eq. (17) of Ref. 16 do not satisfy the Ward identity for λ_T , nor do they exhibit the required divergence of λ_T , the expected divergence of λ_{TL} , or the expected form for the divergence of λ_L .] Given this simple example, the general expectation of divergent coupling constants when $\chi=0$, and the smooth behavior of the equation of state obtained by Schäfer and Horner, it appears that divergent (renormalized) coupling constants do not constitute compelling evidence for any essential nonanalyticity of the equation of state.

The divergences at the coexistence curve quoted in this paper are a result of the long-range fluctuations of the Goldstone modes, which are in turn a consequence of the breaking of the continuous symmetry of the $O(n)$ vector model. It has been shown by Hilhorst³⁷ that a model which appears to have only hypercubic symmetry is equivalent to polymers in the limit $n \rightarrow 0$. Gujrati argues,¹⁶ based on this fact, that Goldstone modes cannot affect the behavior of polymers because they are not expected in this hypercubic model and that therefore some transition for $H > 0$, $T < T_c$ is a logical necessity. This argument, however, is fallacious for two reasons. First, the Hilhorst model in fact has $O(n)$ symmetry in this limit. To see this, note that the Hamiltonian of the Hilhorst model is itself $O(n)$ symmetric whereas, for $n \neq 0, 1$, the directions in which the spins can point (along the axes) is not. However, the results for the angular, which the spins can point (along the axes), is not. However, the results for the angular average of products of spins at a site are equal in the limit $n \rightarrow 0$ for $O(n)$ and n -hypercubic symmetries.

The second reason is that for $n \neq 0, 1$ the hypercubic model does not possess a simple interpretation as a polymer solution consisting of polymers made up of a single monomer species. For general positive integer n the $O(n)$ model has a consistent interpretation as a model of n species of ring polymers (corresponding to the n -spin components, $\alpha=1, \dots, n$) and one species of chain polymer (corresponding to $\alpha=1$, the direction of the field), all in chemical equilibrium, and such that the interaction energy or excluded volume is the same when unlike polymer species (corresponding to different spin-components α) meet at a site as when like species do. Thus the n -ring species can consistently be thought of as a single species with activity n . As a consequence the n -vector model can be thought of, even for noninteger n , as a multicomponent solution of chains and rings, made up of a single species of monomer, with a specified activity and statistical

weight for each size of ring and chain. In the limit $n \rightarrow 0$ the activity of rings vanishes and only chains survive. It is therefore reasonable to hope to continue the $O(n)$ model in n through $n=1$ to obtain sensible results at $n=0$. In contrast, the hypercubical model of Hilhorst for integer $n > 1$ corresponds to a model of chains and n species or rings in which polymers of different species *completely exclude* each other from the same site, while polymers of the same species only *partially exclude* each other from the same site. In the condensed phase where chains are present, the chains will favor one species of ring over the others, and this will lead to behavior characteristic of $n=1$ rather than $n > 1$. Moreover, there is no natural way to extend the interpretation of this polymer model, in which the n -ring species distinguish each other from themselves, to noninteger n . It thus seems clear, therefore, that while the Hilhorst model may be a useful computational device in the limit $n \rightarrow 0$, its hypercubical nature for $n > 0$ should not be used to argue about the expected behavior of polymers.

VI. POLYMERS AND THE ORDER OF LIMITS

In the above we have implicitly taken the thermodynamic ($V \rightarrow \infty$) limit before the limits $n \rightarrow 0$ or $h \rightarrow 0$. In Sec. VI of Ref. 16, it is argued that for $n=0$ the limits $H \rightarrow 0$ and $V \rightarrow \infty$ can be interchanged. This conclusion is technically in error, although the example adduced by Gujrati is interesting in that it illustrates the rather complex dependence of results in the $n \rightarrow 0$ vector model on the order of the limits $V \rightarrow \infty$, $n \rightarrow 0$, and $H \rightarrow 0$. If one takes the limit $n \rightarrow 0$ before the limit $V \rightarrow \infty$, then $\lim_{H_0 \rightarrow 0} \lim_{V \rightarrow \infty} \neq \lim_{V \rightarrow \infty} \lim_{H_0 \rightarrow 0}$, in agreement with the assertion by Parisi and Sourlas.³⁸ The reason is that for the one-dimensional n -vector model considered by Gujrati, the *multiplicity* of the eigenvalue λ_2 is n so that the partition function is

$$Z \approx \lambda_1^N + n\lambda_2^N + \cdots, \quad (51)$$

where $N \propto V$ is the number of lattice sites. If the limits are taken in the order (working from right to left) $\lim_{V \rightarrow \infty} \lim_{H_0 \rightarrow 0} \lim_{n \rightarrow 0}$ or $\lim_{V \rightarrow \infty} \lim_{n \rightarrow 0} \lim_{H_0 \rightarrow 0}$ then the second term in Eq. (51) contributes nothing and λ_1 tends to unity before $N \rightarrow \infty$ so that $Z \equiv 1$ and no phase transition results. However, if the limits are taken in the order $\lim_{H_0 \rightarrow 0} \lim_{V \rightarrow \infty} \lim_{n \rightarrow 0}$ we³⁹ and others⁴⁰ have shown earlier that a phase transition occurs at $K=1$ to a polymerized state consisting of an infinite number of polymer chains. The thermodynamic potential in the limit $H_0 \rightarrow 0$ is given by [Gujrati's K is identical to \tilde{J} in Eq. (32)]

$$-\frac{F}{k_B T} = \lim_{H_0 \rightarrow 0} \lim_{N \rightarrow \infty} \lim_{n \rightarrow 0} N^{-1} \ln Z = \begin{cases} \ln K & (K \geq 1) \\ 0 & (K \leq 1). \end{cases} \quad (52)$$

It is possible to obtain a phase transition to a polymerized state with $H_0=0$ before $V \rightarrow \infty$ provided the limit $n \rightarrow 0$ is taken *after* the thermodynamic limit. With the order of

limits $\lim_{n \rightarrow 0} \lim_{V \rightarrow \infty} \lim_{H_0 \rightarrow 0}$, the second term in Eq. (51) dominates for $K > 1$, and $Z \sim n\lambda_2^N$ for all $n > 0$. The thermodynamic limit then gives the free energy per spin F

$$-\frac{F}{k_B T} = \lim_{n \rightarrow 0} \lim_{N \rightarrow \infty} \lim_{H_0 \rightarrow 0} N^{-1} \ln Z = \begin{cases} \ln K & (K \geq 1) \\ 0 & (K \leq 1). \end{cases} \quad (53)$$

Although this free energy is the same as that in Eq. (52), the resulting polymerized state is quite different from that obtained with the order of limits in Eq. (52). There the polymeric state consists of an infinite number of open chains, whereas here it consists of a single closed ring comprising the entire lattice. [We have assumed periodic boundary conditions. If free boundary conditions are used then no phase transition occurs even for the order of limits in Eq. (53).]

This sensitive dependence of the thermodynamic state upon the order of limits is expected to be more general than the one-dimensional example considered in Ref. 16. We have argued elsewhere^{21,22} that the equilibrium polymerization of chains and rings together has aspects of bicriticality; that it is a crossover point between the polymerization transition to chains described by the $n=0$ vector model and a polymerization to an infinite ring condensate described by the $n=1$ vector model in the limit that $H \rightarrow 0$ before $V \rightarrow \infty$. We expect in general, for $d > 2$,⁴¹ that the order of limits $\lim_{n \rightarrow 0} \lim_{V \rightarrow \infty} \lim_{H \rightarrow 0}$ will produce a polymerized state consisting of infinite rings (rings of size bounded only by the requirement that their radius of gyration cannot exceed the size of the vessel), whereas the orders of limits $\lim_{n \rightarrow 0} \lim_{H \rightarrow 0} \lim_{V \rightarrow \infty}$ or $\lim_{H \rightarrow 0} \lim_{n \rightarrow 0} \lim_{V \rightarrow \infty}$ or $\lim_{H \rightarrow 0} \lim_{V \rightarrow \infty} \lim_{n \rightarrow 0}$ will all produce a state completely dominated by chain polymers. While the zero-field free energy may be the same for these states, they can be distinguished by different values of the derivative with respect to an anisotropy field^{21,22} in the limit of zero anisotropy field and zero magnetic field, corresponding to the distinction between the fraction of monomers in polymer rings and in polymer chains. Finally, no polymers are present if the limit $V \rightarrow \infty$ is taken after the limits $n \rightarrow 0$ and $H \rightarrow 0$.

It is worth emphasizing that with $\lim_{H_0 \rightarrow 0}$ taken after $\lim_{V \rightarrow \infty}$ the polymerized state consists of an *infinite* number of polymerized chains even though the concentration of chains x_p vanishes as $H_0 \rightarrow 0$, whereas with $\lim_{V \rightarrow \infty}$ after $\lim_{H_0 \rightarrow 0}$ there are *no* chains present even for $K > K_c$. As noted above, moreover, with $\lim_{V \rightarrow \infty}$ first, the number of other polymers that visit the volume occupied by a single polymer *diverges* for $H_0 \rightarrow 0$ with $K > K_c$. While it may be possible by *coupling* the limits $V \rightarrow \infty$ and $H_0 \rightarrow 0$ to obtain a state with only a single polymer chain occupying a nonzero fraction of the lattice sites as discussed recently,¹⁷ this should be viewed as a highly unusual crossover between the two conventional limits. It appears that for most practical considerations the order of limits $V \rightarrow \infty$ before $H_0 \rightarrow 0$ is the limit of interest. For example, in the case of sulfur we have estimated²² that the infinite-vessel limit is approached for containers larger than a few hundred angstroms.

VII. DISCUSSION

We have shown that the equation of state for the n -vector model given by Schäfer and Horner can be put in a parametric form proposed by Schofield, Litster, and Ho that is manifestly analytic to order ϵ^1 even for $n < 1$ throughout the H - T plane in the neighborhood of the critical point except for the critical point itself and the coexistence curve. This is at variance with the claim by Gujrati that a singularity occurs for $H > 0$, $T < T_c$ signaling the appearance of a new "collapsed" phase. We have also shown that the equation of state of Lawrie is not manifestly inconsistent with this analyticity, as claimed by Gujrati. These findings, of course, neither prove the analyticity of the free energy nor disprove the possibility of a collapsed phase, any more than ϵ expansion results "prove" the existence of power laws or scaling for $n \geq 1$. We do conclude, however, that there is no evidence for the nonanalyticity claimed by Gujrati nor for the collapsed state proposed by him in any of the published equations of state of Schäfer and Horner,²⁵ Lawrie,²⁴ or Knoll, Schäfer and Witten.⁴ Rather, the evidence suggests that the equation of state for equilibrium polymerization of chain polymers, as determined by the $n \rightarrow 0$ vector model is well behaved except in the limit $K_1 = \frac{1}{2}h^2 \rightarrow 0$ for $K_p' \geq (K_p')^c$ ($T \leq T_c$ for the magnet). In particular, the conditions for thermodynamic stability of the polymer system are satisfied everywhere in the vicinity of the critical point. The order of the limits $n \rightarrow 0$, $H \rightarrow 0$, $V \rightarrow \infty$ is subtle, but as long as $H \rightarrow 0$ is taken after $V \rightarrow \infty$ it is expected that the results are independent of other orderings of the limits for physical systems with $d > 2$.

It is instructive to compare the results obtained here with those for the exact solution of the $n \rightarrow 0$ vector model in the mean-field approximation obtained earlier.⁸ These differ in two respects. The results here contain terms proportional to ϵ not contained in the mean-field results, whereas the exact mean-field solution contains *correction to scaling* terms not included here. However, setting $\epsilon = 0$ in our scaling equation and retaining only the scaling terms in the mean-field solution, one obtains complete agreement. In particular, one finds from Eqs. (1), (8), and (19)–(24) that $C_m = (\partial e / \partial \tau)_m = 0(\epsilon)$, in agreement with the mean field result $C_m = 0$. Similarly, one finds from Eq. (8) with $\epsilon = 0$ that $\chi = \frac{1}{2}r^{-1}$, in exact agreement with the scaling limit of the exact mean-field solution. (It is necessary to recognize that in Ref. 8 a different scaling of m and h is used requiring $m_0 = 2$, $a = 4$, but this does not affect the result for χ .) Thus, near the critical point $\chi > 0$ in the mean-field approximation. Farther from the critical point one finds in the mean-field approximation a locus where $\chi = 0$. That locus divides the h, τ plane into a region of negative susceptibility at large values of $|h|$ and low temperatures, and a region of positive χ for small h and high temperature. In the notation used here that locus is given by⁸ $|h| = 2^{-1/2}(1 + \tau)$. In Fig. 1 we show this locus as well as the scaling curves $\theta^2 = \theta_0^2$ along which $\chi = 0$ from Eq. (8). Negative susceptibility at large h is expected to be quite general, not just a feature of mean-field theory. It arises from the physical requirement that $x_p = \frac{1}{2}hm$ is bounded as $h \rightarrow \infty$, requir-

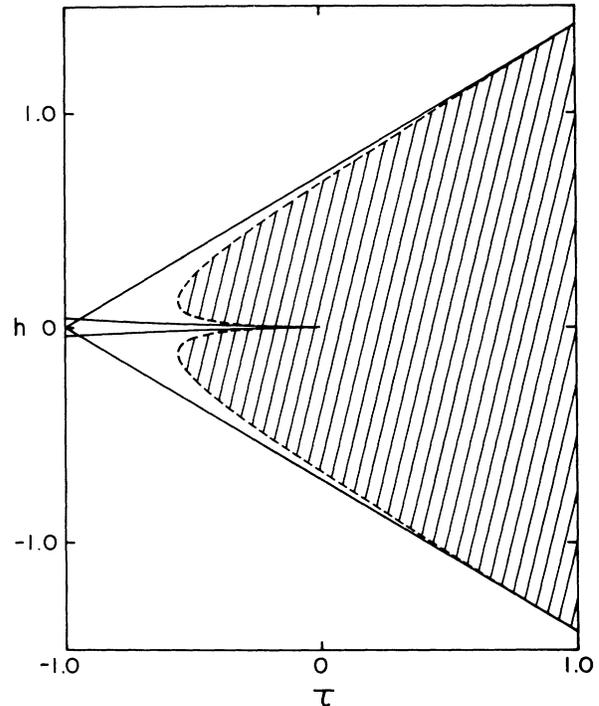


FIG. 1. Locus of $\chi=0$ in the $n \rightarrow 0$ vector model. The straight lines $|h| = 2^{-1/2}(1 + \tau)$ give the locus $\chi=0$ in the mean-field approximation. The solid curves indicate the locus according to our scaling equation of state. The dashed curves indicate qualitatively a plausible conjecture for the locus $\chi=0$ when both fluctuations and corrections to scaling are taken into account. The shaded region is the region of positive χ corresponding to this conjecture.

ing that m decrease with increasing h for large h . This leads naturally to the conjecture that the actual shape of the locus $(\partial m / \partial h)_\tau = 0$ when correction to scaling contributions are included will be given qualitatively by the dashed curves in Fig. 1. This is different from the shape proposed in Fig. 3 of Ref. 8, where the correct scaling nature of the curves was deduced but they were incorrectly supposed to leave the critical point immediately toward higher temperature rather than first descending to lower temperature. The region where χ is expected to be positive is shaded in Fig. 1.

Consider, then, what is known from the mean field and ϵ -expansion results together with the exact correspondence between polymers for $n \rightarrow 0$. First, there is an exact formal correspondence between the partition functions of the $n \rightarrow 0$ vector model and equilibrium polymerization of chains. Second, within the mean-field approximation for the $O(n)$ vector model the susceptibility is negative for large h and low T and positive for small h and high T , but thermodynamic stability is satisfied for the corresponding polymer solution *through the entire h - T plane* and the corresponding polymer solution is described *exactly* by the physically sensible Tobolsky-Eisenberg theory of equilibrium polymerization throughout the entire h - T plane. In particular, no physical singularity arises in the

polymer language upon crossing the locus $\chi=0$. Our results here are completely consistent with the picture that critical fluctuations change the situation only by changing the *shape* of the region of negative χ so that it includes a wedge-shaped portion extending to the critical point along the coexistence curve, as in Fig. 1, and by allowing for $\chi \rightarrow -\infty$ along the coexistence curve. It remains the case that no physical singularity arises in the polymer language at the locus $\chi=0$ and that stability is satisfied in the polymer language throughout the h - T plane, at least in the vicinity of the critical point, which is all that a scaling equation of state can investigate.

Apart from its utility in addressing the behavior of polymers, we believe that the strategy employed in the parametric form of the equation of state proposed in Eqs. (1)–(3) may be more generally useful. The Schofield-Ho-Litster form has the advantage that the analyticity of

the equation of state is easily seen and that thermodynamic derivatives are easy to calculate using Jacobians. In addition, it provides a convenient parametrization of the many different ways of expressing scaling in polymer solutions.

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