

Polymer statistics, the n -vector model, and thermodynamic stability

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The scaling hypothesis is now widely used in polymer statistics because of the correspondence between this problem and the $n \rightarrow 0$ limit of the n -vector model of magnetism. We prove here that if the $n \rightarrow 0$ vector model satisfies scaling, then its free energy does not always satisfy the usual convexity requirements of thermodynamic stability, even above the critical temperature in small fields. We also show that, because of the very different role played by the field variables in the two interpretations, the corresponding model of polymer solutions does not suffer from this instability.

Scaling ideas have proven very useful in the understanding of polymers and polymer solutions.^{1,2} The necessity in polymer statistics for nonclassical exponents in order to account for deviations from Gaussian behavior was recognized early by Flory,³ and calculations of these exponents by self-consistent approximation methods^{4,5} and by direct counting of walks on lattices⁶⁻¹⁰ have yielded estimates of increasing reliability. The introduction of scaling ideas and the widespread recognition of the intimate connection between polymer statistics and critical phenomena came only later, with the recognition by De Gennes¹¹ that the statistics of a single polymer chain is related to the behavior of the isotropic n -vector model of ferromagnetism in the special limit $n \rightarrow 0$. This correspondence was extended by Des Cloizeaux¹² to the case of polymers in solution, where interactions between different polymers must be considered. The result of this work has been the application of the scaling hypothesis,^{13,14} already well established for critical phenomena, to polymer statistics. This development has been rather successful, as shown by experiments² and as summarized in a recent book by De Gennes.¹

However, scaling is still a hypothesis, and although other arguments can be given to motivate the use of scaling concepts in polymer physics,¹ one of the most compelling arguments remains the connection with the n -vector model. This argument rests on the fact that the n -vector model is now believed¹⁵ to obey scaling for n having physical values 1, 2, 3, and is *presumed* to obey scaling even when n is continued to $n \rightarrow 0$. In this note we point out that there is a curious feature in this argument. We show that if scaling is assumed for the $n \rightarrow 0$ limit of the n -vector model, then the resulting magnetic free energy necessarily fails to satisfy the usual convexity require-

ments of thermodynamic stability as the critical point is approached from temperatures above T_c along certain scaling curves on which the magnetic field vanishes as $T \rightarrow T_c$. This observation might appear, at first, to invalidate the whole scaling picture of the polymer problem. However, when stability of the polymer problem itself is considered, using only polymer variables, stability is recovered and no drastic consequences of scaling are found. This results from the very different role played by the independent field variables in the magnetic and polymer problems. One is thus in the somewhat curious position that there is no internal thermodynamic inconsistency in postulating the scaling equation of state for polymers, but that the rigorous correspondence between the two models means that this postulate implies a thermodynamically unacceptable free energy for the $n \rightarrow 0$ limit of the n -vector model. Were the $n \rightarrow 0$ limit a physically realizable magnetic system, this would be sufficient reason to rule out scaling in the polymer problem. However, given the artificial and non-physical nature of the $n \rightarrow 0$ limit, one may reasonably argue that this should not exclude the use of scaling for polymers.

We use the correspondence between the $n \rightarrow 0$ limit of the n -vector model on a lattice and the statistics of self-avoiding walks on a lattice employed by G. Sarma, both in the Appendix of Ref. 2 and in a more recent review.¹⁶ (An earlier treatment by Bowers and McKerrell¹⁷ uses a different normalization of the spins and fields.) Consider the n -vector model on a d -dimensional lattice of volume V with Hamiltonian

$$\mathcal{K} = -J \sum_{RR'} \vec{S}_R \cdot \vec{S}_{R'} - m_0 H \sum_R S^{(1)}(R), \quad (1)$$

where the sum $\sum_{RR'}$ is over all distinct nearest-neighbor pairs of spins and where S is a class-

ical spin with magnetic moment m_0 and norm \sqrt{n} as follows:

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

and $S^{(\alpha)}$ is its component parallel to the field H . In the limit $n \rightarrow 0$ the partition function Z and free energy (Ref. 18) F of this model are related to the polymer statistics by the equation¹⁶

$$Z = e^{VF} = \sum_{N_m, N_p} \beta^{N_m} h^{2N_p} \Gamma(N_p, N_m, V), \quad (3)$$

where

$$\beta = \frac{J}{kT}, \quad h = \frac{m_0 H}{kT}, \quad (4)$$

and where $\Gamma(N_p, N_m, V)$ is the number of ways to put N_p self-avoiding walks (polymers with excluded volume) containing a total number N_m of monomers (bonds or steps) onto a lattice of V/v_0 sites, where v_0 is the volume per site.

The concentration of polymers, c_p , and of monomers contained in polymers, c_m , is related to Z (or F) through

$$2c_p = \frac{2\langle N_p \rangle}{V} = \frac{1}{V} h \left(\frac{\partial \ln Z}{\partial h} \right)_\beta, \quad (5)$$

$$c_m = \frac{\langle N_m \rangle}{V} = \frac{1}{V} \beta \left(\frac{\partial \ln Z}{\partial \beta} \right)_h,$$

while the (dimensionless) magnetization density m and configurational energy density e for the magnet are given by

$$m = \frac{\langle M \rangle}{V} = \frac{1}{V} \left(\frac{\partial \ln Z}{\partial h} \right) = \frac{\langle \sum_{\mathbf{R}} S_{\mathbf{R}}^{(1)} \rangle}{V}, \quad (6)$$

$$e = \frac{\langle E \rangle}{V} = \frac{1}{V} \left(\frac{\partial \ln Z}{\partial \beta} \right) = \frac{\langle \sum_{\langle \mathbf{R}\mathbf{R}' \rangle} \vec{S}_{\mathbf{R}} \cdot \vec{S}_{\mathbf{R}'} \rangle}{V}.$$

For the polymer variables N_m and N_p , the "thermodynamic" stability condition corresponds to the observation that, for all real a and b ,

$$\langle (a\Delta N_m + b\Delta N_p)^2 \rangle \geq 0, \quad (7)$$

where

$$\Delta N_m = N_m - \langle N_m \rangle, \quad (8)$$

$$\Delta N_p = N_p - \langle N_p \rangle.$$

Minimizing the left side of Eq. (7) with respect to a at fixed b leads to the requirement that

$$A \equiv \frac{4}{V^2} [\langle (\Delta N_m)^2 \rangle \langle (\Delta N_p)^2 \rangle - \langle \Delta N_m \Delta N_p \rangle^2] \geq 0, \quad (9)$$

together with

$$\langle (\Delta N_m)^2 \rangle \geq 0$$

or

$$(10)$$

$$\langle (\Delta N_p)^2 \rangle \geq 0.$$

Using standard procedures for calculating fluctuations in statistical mechanics,¹⁹ together with Eq. (3), the expression for A can be rewritten in the form

$$A = 2c_m c_p + c_m h^2 \left(\frac{\partial^2 F}{\partial h^2} \right)_\beta + 2c_p \beta^2 \left(\frac{\partial^2 F}{\partial \beta^2} \right)_h + \beta^2 h^2 B, \quad (11)$$

where

$$B = \left[\left(\frac{\partial^2 F}{\partial \beta^2} \right) \left(\frac{\partial^2 F}{\partial h^2} \right) - \left(\frac{\partial^2 F}{\partial \beta \partial h} \right)^2 \right]$$

$$= \frac{1}{V^2} [\langle (\Delta E)^2 \rangle \langle (\Delta M)^2 \rangle - \langle \Delta E \Delta M \rangle^2]. \quad (12)$$

The thermodynamic stability condition for the magnetic n -vector model analogous to (9) and (10) is that F be convex in β and h together, i.e., that

$$B \geq 0 \quad (13)$$

and

$$\frac{\langle (\Delta M)^2 \rangle}{V} = \left(\frac{\partial^2 F}{\partial h^2} \right)_\beta \geq 0$$

or

$$\frac{\langle (\Delta E)^2 \rangle}{V} = \left(\frac{\partial^2 F}{\partial \beta^2} \right)_h \geq 0. \quad (14)$$

What we shall now show is that for scaling equation of state that satisfies the requirements of the $n \rightarrow 0$ limit of the n -vector model, the magnetic stability condition $B \geq 0$ is violated in the vicinity of the critical point with $T \geq T_c$, although the polymer stability condition $A \geq 0$ is satisfied.

The scaling hypothesis made for the $n \rightarrow 0$ limit of the n -vector model, and thus the polymer scaling hypothesis, is that, close to the critical point, the free energy F in Eq. (3) can be written as the sum of singular and more regular parts with the singular part, F_s , satisfying the scaling form

$$F_s(\lambda\tau, \lambda^\Delta h) = \lambda^{2-\alpha} F_s(\tau, h), \quad (15)$$

where $\tau = (\beta_c - \beta)$ and $\lambda > 0$ is a variable parameter, and where the exponents α and $\Delta = \beta\delta$ are among the conventionally defined nonclassical critical exponents.²⁰ A recent estimate²¹ for the n -vector model for $n \rightarrow 0$ gives $\alpha = 0.236$ and $\Delta = 1.46$. (Here we have used the scaling relation $\beta\delta = \gamma + \beta = 2 - \alpha - \beta$.) To write Eq. (15) with $\tau = \beta - \beta_c$ it is necessary that β_c is finite ($T_c > 0$). This is well established.^{17,22} Examination of the high-temperature, zero-field susceptibility series resulting from Eq. (3) shows that the susceptibility is positive and finite for small β and diverges to $+\infty$ at $\beta = \beta_c = 1/\mu$, where

$$\mu = \lim_{N_m \rightarrow \infty} \lim_{V \rightarrow \infty} [\Gamma(N_p = 1, N_m, V)/V]^{1/N_m}. \quad (16)$$

From Table I of Ref. 9, this gives $\beta_c \approx 0.2135$ for the simple cubic lattice. It is reassuring that this value fits well with the values for $n = 1, 2, 3$, as estimated from Fig. 14.1 of Ref. 15 and in Ref. 22.

For $\tau > 0$ ($T > T_c$) the scaling hypothesis may be rewritten in the convenient form

$$F_s = \tau^{2-\alpha} f(h/\tau^\Delta), \quad (17)$$

where the scaling function $f(x)$ is defined on $(-\infty, \infty)$. The singular part of the free energy is generally assumed to be analytic for $T > T_c$ in the vicinity of $h = 0$, from which it follows that $f(x)$ is analytic in some region about $x = 0$. It is an even function of x , and so possesses the expansion

$$f(x) = c + ax^2 + bx^4 + \dots, \quad (18)$$

where the coefficients c, a, b , etc., are all functions of n . The peculiar features of the $n \rightarrow 0$ limit is that c is zero [$c \sim n + O(n^2)$] while a, b , etc., remain nonzero so that

$$f(x) = ax^2 + bx^4 + \dots \quad (19)$$

The vanishing of c is necessary if the model is to give sensible results for polymers (it is required if the osmotic pressure is to vanish as the concentration of polymers vanishes). Moreover, the vanishing of c and nonvanishing of a in the $n \rightarrow 0$ limit follow from arguments based on the $h \rightarrow 0$ limit of the series in Eq. (3) when viewed as a high-temperature series. $F(\tau, h = 0)$ is found to vanish identically for $\tau > 0$ (it is proportional to n as $n \rightarrow 0$), whereas $(\partial^2 F / \partial h^2)_\tau$ is nonzero for $\tau > 0$ and diverges to $+\infty$ at $\tau = 0$. The vanishing of $F(\tau, h = 0)$ for $\tau > 0$ leads, in the magnetic language, to a ratio A^+/A^- of the amplitudes of the specific heat above and below T_c that vanishes in the $n \rightarrow 0$ limit. Brezin *et al.*²³ have calculated A^+/A^- for the n -vector model, to order ϵ , as follows:

$$A^+/A^- = 2^d(1 + \epsilon)n/4 + O(\epsilon^2), \quad (20)$$

which has the appropriate limit as $n \rightarrow 0$.

If we examine the free energy F or its derivatives with respect to β and h using the expansion in Eq. (19) we find that, as $T \rightarrow T_c$ with $x = h/\tau^\Delta$ fixed and small, the first term from Eq. (19) dominates. Accordingly, we may calculate the derivatives in Eqs. (11) and (12) using the free energy

$$F_s = a\tau^{2-\alpha-2\Delta}h^2 + \dots \quad (21)$$

We then easily obtain

$$B = 2a^2\gamma(1-\gamma)\tau^{-(\gamma+\alpha)}x^2 + \dots, \quad (22)$$

where $x = h/\tau^\Delta$, and we have used the scaling relation

$$\gamma = 2\Delta + \alpha - 2 \approx 1.16. \quad (23)$$

We see that B is negative sufficiently close to T_c whenever γ is greater than unity ($\gamma = 1$ is the Gaussian result and all estimates of γ for the polymer problem give $\gamma > 1$). In fact, B diverges to $-\infty$ as T_c is approached along the scaling curve $h/\tau^\Delta = x$ for x fixed and sufficiently small. Thus, if scaling is satisfied for the n -vector model with $n \rightarrow 0$, then thermodynamic stability is violated.

For the polymer problem, however, we obtain for A , in Eq. (11),

$$A = 4a^2\beta_c^2\gamma\tau^{-2\alpha}x^4 + \dots, \quad (24)$$

where the remaining terms of order x^4 contain higher powers of τ (e.g., $\tau^{2\Delta-\alpha}$, $\tau^{3-2\alpha}$, etc.) and are, moreover, positive. In addition, of course, there are also higher-order terms in x (x^6 , x^8 , etc.). The leading term is positive and is the result of contributions from the third and fourth terms on the right-hand side of Eq. (11). The fourth term is negative, as shown above, but the third is positive and larger in magnitude.

The origin of the difference between the magnetic and polymer models is the very different role played by β and h in these two interpretations. For the magnet, β and h play a role analogous to that of chemical potentials, μ_i , (more precisely, to that of μ_i/kT) in the grand canonical ensemble, while in the polymer problem they play a role analogous to that of activities, $z_i = \exp(\mu_i/kT)$. It is this difference that results in the "additional" first three terms in Eq. (11) which save the polymer problem from instability.

It should be noted that scaling and convexity are quite distinct mathematical properties. There is no mathematical requirement that a function which satisfies scaling also be convex. The requirement that F be convex in β and h for magnetic systems is based on physical arguments that are compelling for physical values of n , i.e., $n = 1, 2, 3$, etc., but need not necessarily have much force in the nonphysical limit $n \rightarrow 0$. The conclusion that nonconvexity of F implies nonpositivity of $\langle (a\Delta M + b\Delta E)^2 \rangle$ for some a, b, β , and h requires that the operators M and E be well defined and that there exist a non-negative probability function on the states of the system. The usual methods for deriving the $n \rightarrow 0$ limit avoid these issues and they remain unresolved at present, although some interesting efforts have been made in this direction.²⁴⁻²⁶

In closing we wish to emphasize that the in-

stability that we have pointed out here occurs for $T > T_c$ near $h = 0$ and is not (at least not obviously) connected with another curiosity of the $n \rightarrow 0$ limit, namely, that ϵ expansion of the susceptibility below T_c near $h = 0$ suggests that stability is violated if $n < 1$.²⁷ That conclusion depends upon the appropriate treatment of the ϵ expansion as well as of the $n \rightarrow 0$ limit and it may be hoped that a satisfactory resolution of that difficulty will be found. (The recent contribution

by M. Moore²⁸ is an interesting step in this direction.) The instability discussed here requires only the assumption of scaling and the behavior required of the $n \rightarrow 0$ limit of the n -vector model.

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- ¹P. G. DeGennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, New York, 1979).
- ²M. Daoud *et al.*, *Macromolecules* **8**, 804 (1975).
- ³P. J. Flory, *J. Chem. Phys.* **17**, 303 (1949).
- ⁴P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, New York, 1953).
- ⁵S. F. Edwards, *Proc. Phys. Soc. London* **85**, 613 (1965); *Natl. Bur. Stand. (U.S.), Misc. Publ.* **273**, 225 (1966).
- ⁶F. T. Wall, S. Windwer, and P. J. Gaus, *Methods Comput. Phys.* **1**, 217 (1963) and references therein.
- ⁷M. E. Fisher and M. F. Sykes, *Phys. Rev.* **114**, 45 (1959).
- ⁸M. F. Sykes, *J. Chem. Phys.* **39**, 410 (1963).
- ⁹D. S. McKenzie, *Phys. Rep.* **27**, 35 (1976). (This review gives many additional references.)
- ¹⁰D. S. McKenzie, *J. Phys. A* **12**, 1267 (1979).
- ¹¹P. G. DeGennes, *Phys. Lett.* **38A**, 339 (1972).
- ¹²J. Des Cloizeaux, *J. Phys. (Paris)* **36**, 281 (1975).
- ¹³B. Widom, *J. Chem. Phys.* **43**, 3898 (1965).
- ¹⁴L. P. Kadanoff, *Physics* **2**, 263 (1966).
- ¹⁵H. E. Stanley, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, New York, 1976), Vol. III, Chap. 7.
- ¹⁶G. Sarma, *III Condensed Matter*, 1978 Les Houches Lectures, edited by G. Toulouse and R. Meynard (North-Holland, Amsterdam, 1979), p. 537.
- ¹⁷R. G. Bowers and A. McKerrill, *J. Phys. C* **6**, 2721 (1973).
- ¹⁸Strictly, our "free energy" F is equal to minus the conventional free energy divided by kT where k is Boltzmann's constant and T is the absolute temperature. It plays the role of the Gibbs potential. It is this thermodynamic potential that must be convex in β and h according to the usual requirements of thermodynamic stability. We shall refer to this potential as the free energy.
- ¹⁹Terrell L. Hill, *Statistical Mechanics* (McGraw-Hill, New York, 1956).
- ²⁰H. E. Stanley, *Phase Transitions and Critical Phenomena* (Clarendon, Oxford, 1971).
- ²¹J. Zinn Justin and J. C. LeGuillou, *Phys. Rev. B* **21**, 3976 (1980).
- ²²P. R. Gerber and M. E. Fisher, *Phys. Rev. B* **10**, 4697 (1974).
- ²³E. Brezin, J. C. LeGuillou, and J. Zinn Justin, *Phys. Lett.* **47A**, 285 (1974).
- ²⁴V. J. Emery, *Phys. Rev. B* **11**, 239 (1975).
- ²⁵P. R. Gerber and M. E. Fisher, *J. Chem.* **63**, 4941 (1975).
- ²⁶D. Jasnow and M. E. Fisher, *Phys. Rev. B* **13**, 1112 (1976).
- ²⁷D. J. Wallace and R. K. P. Zia, *Phys. Rev. B* **12**, 5340 (1975).
- ²⁸M. A. Moore and C. A. Wilson, *J. Phys. A* **13**, 3501 (1980).