Behavior of polymer end-to-end distance in two dimensions at the theta point[a)]

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The end-to-end distance of a flexible polymer in a theta solvent in two dimensions is investigated. A mean field theory is presented which predicts significant deviations from ideal behavior at the theta point. A real space renormalization group approach is employed to investigate further the behavior of the polymer's end-to-end distance at the theta point and to elucidate the analogy with thermodynamic tricritical behavior. Our results suggest that the correct result may be numerically closer to the mean prediction than to the values obtained from second order $\epsilon = (3-d)$ expansions of field theory models of critical phenomena.

I. INTRODUCTION

In good solvents polymer molecules are swollen compared to an ideal random coil configuration as a result of excluded volume interactions. At a particular temperature (or change in composition of a mixed solvent), it is possible for this excluded volume effect to vanish, resulting in the polymer chain adopting a more nearly ideal conformation. The point at which such shrinking occurs is referred to as the theta point and roughly corresponds to the Boyle point of a real gas.

The responsible polymer chemist would define the theta point for a dilute solution of monodisperse polymer chains as the point where the mean square end-to-end distance $\langle R^2\rangle_0$ conforms to the classical random walk prediction for dependence on length

$$\langle R^2\rangle_0 = a^2 N \ , \tag{1.1}$$

where a is the segment length and N the number of monomer units in the chain.

In a good solvent, the mean square end-to-end distance of the polymer chain in d-dimensions may be expressed as

$$\langle R^2\rangle = a^2 N^{2\nu(d)} \ , \tag{1.2}$$

where $\nu = \nu(d)$ is the exponent that characterizes the expansion of the chain. From Flory's classical argument[1,2] or more recent modern generalizations, one expects

$$\nu(d) = 3/(d+2) \ , \quad d \le 4 \tag{1.3}$$

apart from logarithmic corrections in N. Above $d = 4$ dimensions the excluded volume effect becomes irrelevant and ν assumes the classical value for ideal chains $\nu = 1/2$. The behavior of polymer chains in good solvents may also be described by analogy to critical behavior in magnetic systems. The application of renormalization group ideas from critical phenomena to the problem of polymer configurations in good solvents was originally suggested by De Gennes.[3]

If one attempts to construct a microscopic theory to explain the transition from the expanded state in a good solvent to the theta point, one immediately encounters new physical behavior that is somewhat unexpected. In particular, one finds that the mechanism which results in ideal behavior at the theta point in three dimensions (vanishing of the effective pair interaction between segments) leads to nonclassical behavior for the mean end-to-end distance in two dimensions. In particular, one finds the index at the theta point depends upon dimensionality and that it deviates from the classical value $\nu' = 1/2$ for $d < 3$. For clarity, the index ν at the theta point is denoted ν'.

There are a number of theories that present predictions for the behavior of $\nu'(d)$. De Gennes,[4] and later Stephen,[5] have argued that the theta point is analagous to a tricritical point of a gas–liquid or magnetic system and employed renormalization group arguments[6] with an expansion in $\epsilon = 3 - d$ to predict for $d \le 3$:

$$\nu'(d) = \tfrac{1}{2} + \frac{8}{3(22)^2}\,\epsilon^2 \ . \tag{1.4}$$

Thus, the ϵ expansion renormalization group result exhibits small, but important, deviations from ideal behavior in two dimensions.

Alternatively, one may employ a generalization of the more conventional Flory type of calculation to arrive at the prediction that for $d \le 3$

$$\nu'(d) = [2/(d+1)] \ , \tag{1.5}$$

so that in two dimensions $\nu'(2) = 2/3$ in sharp contrast to the ϵ-expansion prediction of the renormalization group treatment based on an analogy to a tricritical point, i.e., ϕ^6 in contrast to ϕ^4 field theory.

The sharp difference between these two predictions for ν' in two dimensions as well as the relatively complex reasoning required to apply the ϵ-expansion renormalization group theory to this problem has motivated us to undertake an alternative approach to this problem. In particular we employ a variation of the real space renormalization group (RSRG) method that has been exploited by several workers[7–10] to examine self-avoiding walk (SAW) models appropriate for the excluded volume regime. We believe this RSRG method sheds considerable light on the nature of the theta point, in particular, the sense in which this transition should be regarded as a tricritical point.

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Application of the RSRG to the problem under consideration here is not unique and permits a good deal more freedom than one would prefer. In order to explore the range of alternative numerical results that may be realized, we present several different variations of the RSRG method.

The results of our calculations, presented below, suggest that ν' in two dimensions lies in the range $0.53 < \nu'(2) < 0.68$. This should be compared to the Flory value $\nu' = 2/3$, the De Gennes result (obtained by an ϵ-expansion to second order) $\nu' = 0.505$, and the experimental value of Vilanove and Rondelez[11] $\nu' = 0.56$ obtained from surface pressure isotherms of Langmuir monolayers. In no case do our results approach the recent prediction of Khokhlov[12] that $\nu'(2) = 3/4$.

The principal conclusion of this initial RSRG application to polymer chains at the theta point is that deviations from the classical $\nu' = 1/2$ may be much more pronounced than indicated by available ϵ-expansion calculations. Indeed, the true value may well approach the simple minded mean field result. We intend to undertake more comprehensive calculations to pursue the precise numerical value predicted by the RSRG method.

The remainder of this paper is organized as follows. In Sec. II the self-consisted Flory type theory for $\nu'(d)$ is presented. Section III is devoted to a brief summary, for the uninitiated, of the application of the RSRG to this problem. Section IV presents RSRG group results for three variations of a simple one variable model, and Sec. V contains results for a two variable model.

II. THE MEAN FIELD ARGUMENT FOR THE FREE ENERGY OF A POLYMER CHAIN

In this section, a generalization of the mean field argument of Flory is presented for conditions appropriate to the theta point and for arbitrary dimensionality. The method is based on finding the most probable conformation of the polymer chain from an approximate free energy. The case $d = 3$ has been explicitly considered by De Gennes[4] and by Orfino and Flory.[13] To our knowledge the result $d \neq 3$ has not appeared in the literature, but it is known.[14]

The average mean square end-to-end distance of a polymer coil, in d-dimensions, may be expressed as[1]

$$\langle R^2 \rangle = \frac{\int dR R^{d+1} \exp[-F(R)/k_B T]}{\int dR R^{d-1} \exp[-F(R)/k_B T]} , \tag{2.1}$$

where $F(R)$ is an approximate free energy which is taken to be

$$\frac{F(R)}{k_B T} = \frac{d}{2} \frac{R^2}{\langle R^2 \rangle_0} + \frac{N}{2} [\rho W_2(T) + \rho^2 W_3(T) + \cdots] . \tag{2.2}$$

The first term in Eq. (2.2) represents the entropy of an ideal random coil with $\langle R^2 \rangle_0$ given by Eq. (1.1). Limitations of this form of the free energy have been discussed by de Gennes and des Cloizeaux.[15,16]

The subsequent terms in Eq. (2.2) describe the effect of excluded volume through a power series in the monomer density. The virial coefficients $W_2, W_3, \ldots$, include the influence of successive intramolecular segment interactions of pairs, triplets, etc. The average monomer density may be written as

$$\rho = k(d) N/R^d , \tag{2.3}$$

where $k(d)$ is a numerical geometric factor.

In pursuing a maximum term method, it is useful to define an effective free energy $G(R)$ that includes the d-dimensional volume element according to

$$\frac{G(R)}{k_B T} = \frac{F(R)}{k_B T} - d \ln R . \tag{2.4}$$

In terms of $G(R)$, $\langle R^2 \rangle$ becomes

$$\langle R^2 \rangle = \frac{\int dR R \exp[-G(R)/k_B T]}{\int dR R^{-1} \exp[-G(R)/k_B T]} . \tag{2.5}$$

We next express the right-hand side of Eq. (2.5) in terms of the dimensionless distance

$$x = R/\langle R^2 \rangle_0^{1/2} , \tag{2.6}$$

which leads to the expression

$$\alpha^2 = \frac{\langle R^2 \rangle}{\langle R^2 \rangle_0} = \frac{\int dx x \exp[-G(x)/k_B T]}{\int dx x^{-1} \exp[-G(x)/k_B T]} , \tag{2.7}$$

where we have introduced the customary expansion factor α. In terms of the dimensionless distance x,

$$\frac{G(x)}{k_B T} = \frac{dx^2}{2} - d \ln x + \frac{d}{2} \ln \langle R^2 \rangle_0 + \frac{N}{2} [\rho W_2 + \rho^2 W_3 + \cdots] \tag{2.8}$$

with

$$\rho = k a^{-d} N^{(1-d/2)} x^{-d} . \tag{2.9}$$

If we assume that $G(x)$ has a sharp minimum at $x = x_0$ so that we may approximate

$$\exp[-G(x)/k_B T] = \delta(x - x_0) , \tag{2.10}$$

it is easy to see, from Eq. (2.7), that $\alpha^2 = x_0^2$. The remainder of our calculation is devoted to determining x_0, or equivalently α, from locating, for different cases of interest, the minimum in $G(\alpha)$.

Minimization of the free energy $G(\alpha)$ leads to the first order condition

$$\alpha^{d+2} - \alpha^d = C_2 N^{(4-d)/2} + C_3 N^{(3-d)}/\alpha^d , \tag{2.11}$$

where

$$C_2 = \left(\frac{k W_2 a^{-d}}{2}\right) , \quad C_3 = (k^2 W_3 a^{-2d}) . \tag{2.12}$$

In good solvents for $d < 4$, the triplet term C_3 is irrelevant, and one recovers the conventional result Eq. (1.3).

Near the theta point, W_2 and hence, C_2 will vanish and it is necessary to retain the C_3 term on the right-hand side of Eq. (2.11). We proceed to examine the consequences of Eq. (2.11) for arbitrary d. For $d \gtrsim 3$, for long chains $N \to \infty$ one obtains $\alpha = N^0$. Thus, to terms of order $\ln N$, one recovers the result that $\nu' = 1/2$. For lower dimensionality $d < 3$, one obtains $\alpha^2 = N^{(3-d)/(d+1)}$

which leads to the principal result of this section [see Eq. (1.5)] $\nu' = [2/(d+1)]$ and

$$\langle R^2\rangle = a^2\left[\frac{k^2 W_3}{a^{2d}}\right]^{1/(d+1)} N^{4/(d+1)} \ . \tag{2.14}$$

This is the Flory type prediction for the mean square end-to-end distance in a theta solvent. It differs considerably from the De Gennes prediction Eq. (1.4). In particular, in two dimensions our result $\nu'(2) = 2/3$ suggests a major deviation from ideal behavior $\nu' = 1/2$, in contrast to the very modest departure from ideal behavior found by De Gennes[4] $\nu'(2) = 0.505$.

At temperatures *below* the theta point, monomer–monomer attraction will dominate and the chain will collapse. In this regime $W_2 < 0$ and for large N, one finds from Eq. (2.11):

$$\alpha^d \sim N^{(2-d)/2} \ , \tag{2.15}$$

so that

$$\langle R^2\rangle = a^2 N^{2/d} \ . \tag{2.16}$$

It follows from Eq. (1.2) that in the collapsed state $\nu = d^{-1}$ so that in two dimensions there is a coincidental equality between the index expected from a Gaussian random walk and the index which arises from the uniform distribution of monomers in a disk of radius R that occurs in the collapsed state.

III. SETTING UP THE REAL SPACE RENORMALIZATION GROUP CALCULATION

For a walk on a lattice, the mean square end-to-end distance is defined by

$$\langle R_N^2\rangle = C_N^{-1}\sum_{\mathbf{R}} R^2 C_N(\mathbf{R}) \sim N^{2\nu}\ (N\to\infty) \ , \tag{3.1}$$

where the value of the index ν depends upon the dimensionality and statistical character of the walk. In Eq. (3.1), $C_N(\mathbf{R})$ is the number of N-stepwalks that terminate at $\mathbf{R}$. The quantity C_N is the total number of N-stepwalks:

$$C_N = \sum_{\mathbf{R}} C_N(\mathbf{R}) \sim \mu^N N^{\gamma-1} \ , \tag{3.2}$$

where μ is the effective coordination number of the lattice.[17] In order to frame the polymer problem in a manner that facilitates application of the RSRG, we define a generating function $\hat{R}^2(p)$ for the mean square end-to-end distance where each step in the walk is weighted by a factor p. Thus,

$$\hat{R}^2(p) = \frac{\sum_N\sum_{\mathbf{R}} p^N R^2 C_N(\mathbf{R})}{\sum_N p^N C_N} = \frac{\sum_N p^N \langle R_N^2\rangle C_N}{\sum_N p^N C_N} \ . \tag{3.3}$$

We evaluate the denominator by replacing C_N by its asymptotic form Eq. (3.2) and replacing the sum over N by an integral. The result is

$$\sum_N p^N C_N \sim (\delta p/p_c)^{-\gamma} \ , \tag{3.4}$$

where

$$p_c = \mu^{-1} \ , \quad \delta p = p_c - p \ . \tag{3.5}$$

The numerator is evaluated in a similar manner with the result

$$\sum_N p^N \langle R_N^2\rangle C_N \sim (\delta p/p_c)^{-(2\nu+\gamma)} \ . \tag{3.6}$$

Thus, one finds

$$\hat{R}^2(p) = (\delta p/p_c)^{-2\nu} \ . \tag{3.7}$$

In the real space renormalization procedure that we shall employ here, a series of transformations

$$p \to p' \ ; \quad L \to L' \tag{3.8}$$

are introduced for the weighting factor p and the lattice scale factor L. This is done so as to make a comparison between the walks on the original lattice L and the equivalent walks on the new lattice with larger lattice spacing L'. The transformation takes the form

$$p' = f(p) \ ; \quad L' = bL \ . \tag{3.9}$$

One determines the fixed point $p^* = p_c$ by the condition

$$p^* = f(p^*) \tag{3.10}$$

and linearizes about this point to determine the critical properties of the walk

$$\delta p' = \lambda(p^*)\,\delta p \ . \tag{3.11}$$

If we apply the transformation Eq. (3.8) near the fixed point, we obtain

$$\hat{R}^2(p') = b^{-2}\hat{R}^2(p) \ . \tag{3.12}$$

But,

$$\hat{R}^2(p') = \left(\frac{\delta p'}{p_c}\right)^{-2\nu} = \lambda^{-2\nu}\left(\frac{\delta p}{p_c}\right)^{-2\nu} = \lambda^{-2\nu}\hat{R}^2(p) \ , \tag{3.13}$$

where use has been made of Eq. (3.11). Comparison of Eqs. (3.12) and (3.13) leads to the result

$$b^2 = \lambda^{2\nu} \tag{3.14}$$

or

$$\nu = \ln b/\ln\lambda \ .$$

We shall employ variations of this simple procedure to the problem at hand in subsequent sections.

The RSRG method was originally developed for critical spin systems.[18] It was originally applied to the polymer SAW problem by Hilhorst[19] through the analogy to the $n = 0$ vector spin model. It has subsequently been applied to a number of SAW problems by Shapiro,[7] Family,[8] de Quieroz and Chavez,[9] and Redener and Reynolds.[10]

IV. ONE PARAMETER RSRG

In this section, we present results for three variations of a simple one parameter model for a polymer at the theta point. Following previous work on the polymer SAW problem,[7–10] we construct the RSRG transformation [Eq. (3.9)] by a decimation procedure for a triangular lattice and by a cell method on the square lattice. Two alternative rules are employed for the square lattice.

A polymer in a good solvent is well represented by a SAW on a lattice. The presence of the effective two-

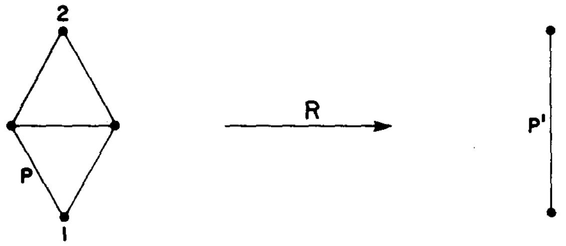

FIG. 1. The transformation of walks on the simplest cluster in the triangular lattice to a single step on the new decimated lattice.

body repulsive potential can be accurately modeled by forbidding a walk to occupy a site or bond more than once.

At the theta point, this effective two body term vanishes, but three body terms remain. To capture this basic feature, we model the polymer by a walk on a lattice that may occupy a bond at most twice. This model has been referred to in the literature as a two-tolerant walk.[20]

For the triangular lattice, an approximate recursion relation is constructed by considering walks within the simplest cluster. Figure 1 represents graphically the transformation for this case. Walks that go from site 1 to site 2 are mapped onto a single step on the new decimated lattice, which has a larger lattice spacing, $L' = \sqrt{3}L$ $(b = \sqrt{3})$.

A typical SAW is shown in Fig. 2(a). This two step-walk is represented by a single step on the new lattice and contributes a weight p^2 to the new weight p'. The recursion relation for the SAW in this lowest approximation is[7]

$$p' = 2p^2 + 2p^3 \ , \qquad (4.1)$$

which has one nontrivial fixed point $P^* = 0.366$ and an eigenvalue determined by linearizing about the fixed point $\lambda = 2.268$. By use of Eq. (3.14) the exponent is determined to be $\nu = 0.671$. This should be compared to the Flory value $\nu = 3/4$.

For a polymer at its theta point, walks that double back on themselves are also allowed. An example is shown in Fig. 2(b), which contributes a term p^4 to p'. Including these walks yields a new recursion relation

$$p' = 2p^2 + 2p^3 + 4p^4 + 6p^5 + 8p^6 \ . \qquad (4.2)$$

There is one nontrivial fixed point for this transformation, $p^* = 0.308$ and an eigenvalue $\lambda = 2.675$. This corresponds to an exponent $\nu' = 0.558$ which, as in the SAW case, is below the simple mean field prediction $\nu' = 2/3$.

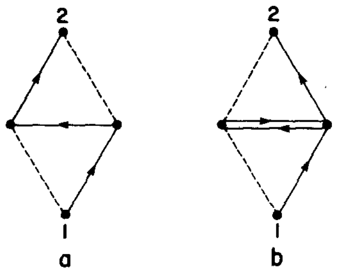

FIG. 2. (a) Example of a SAW contributing to p'. (b) Example of a polymer configuration at the theta point which contributes to p'.

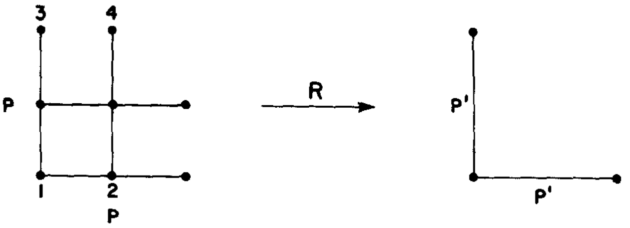

FIG. 3. Transformation of a 2×2 cell to a renormalized horizontal and vertical bond.

In the case of the square lattice, we divide the lattice into cells which preserve the symmetry of the original lattice. We treat here the simplest case of a 2×2 cell, which has a scaling factor $b = 2$. Figure 3 shows graphically the transformation for this case. We consider two possible rules for counting walks that have been previously employed for SAW.[8–10] In the first method, one counts walks that start at site 1 (Fig. 3) and traverse the cell to site 3 or 4 (or the equivalent horizontal positions). These walks are mapped onto a single step on the new lattice.

An alternative (method II) is to count all walks that traverse the cell. Thus, walks are allowed to start at either site 1 or 2. For larger cells, both methods should converge to the same result.

The recursion relations for the SAW for the two rules are[8–10]

$$p' = p^2 + 2p^3 + p^4 \quad \text{(method I)}$$

and (4.3)

$$p' = 2p^2 + 4p^3 + 2p^4 \quad \text{(method II)} \ .$$

These both yield one nontrivial fixed point,

$$p^* = 0.466 \ , \quad \lambda = 2.636 \quad \text{(method I)}$$

and (4.4)

$$p^* = 0.297 \ , \quad \lambda = 2.457 \quad \text{(method II)} \ ,$$

and values for the exponent $\nu = 0.715$ and $\nu = 0.771$, respectively. De Queiroz and Chaves[10] have reported calculations up to $b = 4$ for the above two methods which appear to be converging to the same value for the exponent. Even in this smallest cell, they are surprisingly close to the Flory value which lies between them.

We construct recursion relations for the polymer at its theta point by allowing double occupancy of a bond. The recursion relation for method I is

$$p' = p^2 + 2p^3 + 3p^4 + 4p^5 + 6p^6 + 8p^7 + 5p^8 \ . \qquad (4.5)$$

This recursion relation has a fixed point at $p^* = 0.381$ and an eigenvalue $\lambda = 3.225$. This yields an exponent for the theta point $\nu' = 0.592$. Alternatively, if we allow the walk to start at site 1 or 2 (method II), we obtain,

$$p' = 2p^2 + 4p^3 + 6p^4 + 8p^5 + 12p^6 + 16p^7 + 10p^8 \qquad (4.6)$$

which has a fixed point $p^* = 0.268$, an eigenvalue

TABLE I. Values of the theta point exponent ν' with $\alpha = 0$ (no free parameter) and with α chosen so that the SAW exponent fits the Flory value (3/4).

	$\nu'(\alpha=0)$	α	$\nu'(\alpha)$
Triangular	0.558	−1.621	0.543
Square (I)	0.592	−0.877	0.591
Square (II)	0.688	1.994	0.681

$\lambda = 2.740$, and the exponent $\nu' = 0.688$. It should be noted, that as in the SAW calculation, the mean field value $\nu' = 2/3$ lies between the two results.

There is a fairly large spread in the values obtained for $\nu'(0.558-0.688)$, but considering the simplicity of the calculation, they are quite reasonable. In light of the accuracy obtained for the SAW exponent for the three calculations, it appears that the mean field result may lie quite close to the actual value of ν'. Calculations with larger clusters or cells are needed to determine accurately the numerical value.

One can imagine *ad hoc* procedures that could be exploited in order to achieve more accurate results or to explore the sensitivity of the procedure. One example of such a procedure that has been introduced in another context[21] is to add an empirical term of the SAW recursion relation

$$p' = f(p) + \alpha p^n \ , \tag{4.7}$$

where the additional term is intended to represent walks not included in the restricted cluster which serves as the basis for construction $f(p)$. The coefficient n is chosen to correspond to the shortest path not included in the adopted cluster; for the case of the triangular lattice considered here $n = 3$ and for the square lattice $n = 4$.

The value of the parameter α is chosen so that the resulting 2-*D* SAW exponent is the Flory value $\nu(2) = 3/4$. For the theta case, the relation Eq. (4.7) is employed with the addition of the new allowed paths and the value of α determined above. A new value of $\nu'(2)$ is determined for this value α. In this way, one has an *ad hoc* procedure for examining the sensitivity of the theta point calculation to the underlying SAW walk description. Results for the square and triangular lattice are presented in Table I. The results suggest that the determined value of ν' may not be very sensitive to the manner in which the walks are enumerated. Of course this method does not prove the point since it is an *ad hoc* procedure. Its *ad hoc* nature is best illustrated by noting that the value of the empirical parameter α is found to be negative in some cases rather than positive as suggested by the heuristic rationale for the procedure.

V. TWO PARAMETER RSRG

In the previous section, we considered three variations of a simple one parameter model to obtain an estimate for the value of ν'. In this section, we adopt a more general model that allows for a variable weight for double occupancy of a bond. We present this calculation to elucidate two qualitative points. The first is that double occupancy belongs to a different universality class than the SAW. If the weight associated with double occupancy is increased relative to single occupancy, a new end-to-end behavior appears in the large N limit. The second is to illustrate the analogy to thermodynamic tricritical phenomena in a more physical manner than the field theoretic approach.[3] Thus, the calculation is not presented only to improve the numerical accuracy of our estimate of the theta point exponent, but also to give a simple picture of the transitions from good solvent to theta solvent to the collapsed state.

For simplicity we consider the triangular lattice only, although similar results can be obtained for the square lattice.[22] We generalize the recursion relation for p' [Eq. (4.2)] by assigning a weight q for bonds that are doubly occupied and p for bonds that are singly occupied. Therefore, the walk depicted in Fig. 2(b) will contribute p^2q to a new singly occupied step on the decimated lattice. This yields a new recursion relation for p,

$$p' = p^2[2 + 4q + 8q^2] + p^3[2 + 6q] \ . \tag{5.1}$$

To obtain a doubly occupied bond on the decimated lattice, a walk must go from site 1 (Fig. 1) to site 2 and return to site 1. Enumerating all such walks yields a recursion relation for q,

$$q' = 2q^2 + 10q^3 + 34q^4 + 34q^5 + p^3[8q + 16q^2] + p^4[2 + 6q] \ . \tag{5.2}$$

The fixed points of this coupled set of parameters are determined from the relations

$$\begin{aligned} p^* &= f(p^*, q^*) \ , \\ q^* &= g(p^*, q^*) \ . \end{aligned} \tag{5.3}$$

These two parameter recursion relations have three nontrivial fixed points labeled A, B, and C in the flow diagram (Fig. 4). The three fixed points control the critical (or large N limit) properties of a polymer in a

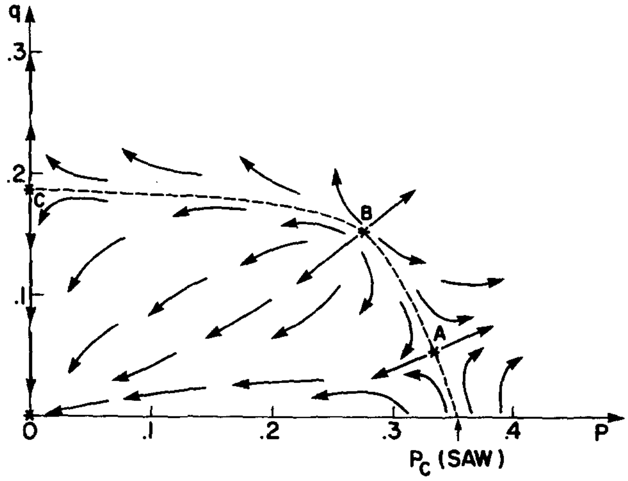

FIG. 4. Qualitative flows for the two parameter recursion relations [Eqs. (5.1) and (5.2)]. The dashed line represents the critical surface on which the three fixed points A, B, and C lie. The fixed points A, B, and C are for the SAW, theta point, and collapsed state, respectively.

TABLE II. Fixed points, eigenvalues, and exponents for the two parameter recursion relations. The three fixed points A, B, and C control the critical properties of a SAW, theta point, and collapsed state, respectively.

Fixed point	p^*	q^*	$\lambda +$	$\lambda -$	ν
A (SAW)	0.333	0.053	2.475	0.531	0.606
B (Theta)	0.279	0.150	2.804	1.560	0.533
C (Collapsed)	0.0	0.188	2.936	0.0	0.510

good solvent, a theta solvent, and a collapsed state,[23] respectively.

To analyze the critical properties of these walks near their respective fixed points, a simple generalization of the one parameter RSRG discussed in Sec. III is employed.[18] We linearize about each fixed point to obtain the local flows,

$$\begin{bmatrix} \delta p' \\ \delta q' \end{bmatrix} = \begin{bmatrix} \lambda_{11} & \lambda_{12} \\ \lambda_{21} & \lambda_{22} \end{bmatrix} \begin{bmatrix} \delta p \\ \delta q \end{bmatrix} . \tag{5.4}$$

Diagonalization of the above 2×2 matrix determines eigenvalues $\lambda_\pm$ which control the divergence of the generating function $\hat{R}^2$. The resulting values for the three fixed points are listed in Table II.

The three fixed points all lie on a single critical surface shown on the dashed line in Fig. 4. On the critical surface, the flows upon renormalizing the walks are away from the theta fixed point B, towards the SAW fixed point A, or the collapsed fixed point C, and from the p axis towards A. The intersection of the critical surface with the p axis corresponds to p_c for the SAW. The fixed point A is off the p axis because we have considered multiple bond occupation.

The flow diagram gives us the following physical picture. A walk with a low weight for double occupancy will, in the large N limit, behave like a SAW. Thus, there is a region corresponding to a good solvent, of double occupancy weight that exhibits the SAW exponent with $\nu = 0.606$. A walk with a large weight for double occupancy compared with single occupancy will be in the collapsed state in the large N limit with $\nu_c = 0.501$. The theta point corresponds to a delicate balance between these two "phases." In our simple model, the weight for double occupancy must be slightly larger than the weight for two single occupied bonds for this to occur. In this manner, the theta point is analogous to a tricritical point. A more quantitative picture can be constructed by considering the eigenvalues of the renormalization group transformation.

Both fixed points A and C have one relevant eigenvalue (i.e., $\lambda_+ > 1$). Along the local axis defined by the corresponding eigenfunction, the flows are away from the fixed point. The other eigenvalue ($\lambda_- < 1$) is associated with an irrelevant parameter. Thus, the large N properties of the walk are insensitive to the precise value of q. There is a region for both the SAW and the collapsed state (i.e., good and poor solvents) in the (p, q) plane that will converge to their respective fixed points for large N. The exponents associated with the fixed points are listed in Table II.

The theta fixed point B has two relevant eigenvalues ($\lambda_\pm > 1$). Thus one must be at both a critical value of p and the proper relative weight q for the corresponding divergence to be seen. The divergence is controlled by the larger of the two eigenvalues. The resulting theta point exponent is $\nu' = 0.533$. The existence of two relevant eigenvalues is analogous to the standard picture of tricritical points for thermodynamic systems.[24]

VI. CONCLUDING REMARKS

In this paper, we have investigated the behavior of the polymer end-to-end distance, at its theta point in two dimensions. Our approach has been to examine the consequences for the end-to-end distance that arise from the vanishing of pair monomer–monomer effective interactions.

Our analysis is based on the real space renormalization group which has been applied here, to our knowledge for the first time, to the theta point. The method permits a description of the polymer in the three possible circumstances of a good solvent, a collapsed state, and the theta point.

The results obtained indicate a value for the critical index at the theta point that is closer to the mean field value than to the value obtained from the $\epsilon = 3 - d$ expansion of de Gennes. Further work is required to determine accurately the precise value of this index. The outcome is not altogether uninteresting. If the correct value turns out to be quite close to $\nu' = 1/2$, as suggested by the ϵ-expansion method, polymer chemists will not be required to modify conventional beliefs about theta point behavior. If the correct value turns out to be closer to $\nu' = 2/3$, some modification of conventional thinking is required, accompanied by considerable satisfaction about the power of Flory type mean field theories in polymer chemistry.

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