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Polymer excluded volume exponent $v$ in three dimensions by direct renormalization

F. Family

Center for Polymer Studies and Department of Physics, Boston University, Boston, Mass. 02215, U.S.A.

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Abstract. — The polymer excluded volume exponent $v$ is calculated using a direct position space renormalization group approach without reference to the zero-component spin model. Self-avoiding-walks (SAW's) and neighbour-avoiding-walks (NAW's) are used as a model of a polymer chain. Renormalization group recursion relations are calculated exactly for cubic cells of linear size 2 and 3. Our results are consistent with the best experimental and theoretical estimates.

1. Introduction. — The mean end-to-end distance $\langle R^2 \rangle^{1/2}$ of a flexible polymer chain in a good solvent varies with the number of monomers $N$ as [1],

$$\langle R^2 \rangle^{1/2} \sim N^v.$$ (1)

The exponent $v$ plays an important role in many aspects of polymer behaviour [1]. Therefore, in the past four decades there have been many attempts to calculate the value of this fundamental quantity (see e.g. McKenzie [2], de Gennes [1] and references therein). However, only recently it has been possible to obtain very accurate values for $v$ in three dimensions both experimentally [3] and theoretically [4].

Much of the recent successes in the study of polymers stems from the important discovery by de Gennes [5] (and its extensions by des Cloizeaux [6]) that self-avoiding-walks SAW's — which may be used to model polymer chains with excluded volume — are equivalent to the $n = 0$ limit of the $n$-vector model. This equivalence allowed many of the powerful techniques of critical phenomena to be applied to polymers [1]. For example, both field theoretic renormalization group (RG) [4] and position space RG (PSRG) [7] (using the Niemeijer-van Leeuwen approach [8]) have been used to study the zero-component spin system. In fact, the theoretical estimate of $v$ in three dimensions with the highest claimed accuracy is obtained by the latter approach [4].

Although the approaches based on the equivalence with the zero-component spin model are elegant and powerful — and in the case of the field theory results highly successful — they lack the transparency of more intuitive and direct methods. Thus, it may be more instructive to apply the renormalization process directly to polymer configurations, where the ideas are more intuitive and the mathematical methods less cumbersome.

A direct PSRG approach for the SAW problem was proposed by Shapiro [9], which does not use the analogy with the spin system. However, Shapiro uses decimation which is known to give relatively poor numerical results. Recently, a cell renormalization transformation is developed for linear polymers [10, 11, 12] and branched polymers [10] in the same spirit as the cell PSRG for percolation [13]. This cell renormalization approach has been successfully used to calculate $v$ in two dimensions for both linear polymers (SAW's) [10, 11, 12] and branched polymers [10]. However three dimensions, where the most accurate numerical estimates for $v$ are given [3, 4], has not been studied previously by this method.

In this article we extend the cell PSRG by calculating the exponent $v$ in three dimensions. Usually the lattice SAW model is used to describe linear polymers in a good solvent. For this reason we first calculate $v$ for the SAW model on a simple cubic...
In addition we also calculate \( v \) for neighbour-avoiding-walks (NAW's) on the square lattice and on the simple cubic lattice. A NAW is a random walk in which there is a larger excluded volume so that — in addition to the usual SAW constraint — the walk may not visit the nearest neighbours of a previously visited site [14]. It is instructive to see how accurately this latter model describes linear polymers.

2. Calculation of the exponent \( v \). — Since the details of the direct cell renormalization approach for polymers has been presented elsewhere [10], we only give a brief outline here. First, we divide the lattice into cells that both cover the lattice and preserve its symmetry. To each walk that enters a given cell from the origin (point \( O \) in figure 1) and spans to the opposite edge of the cell we associate a weight (or fugacity) \( p' \), where \( n \) is the number of steps in the walk. All spanning walks are mapped to a single step on a renormalized lattice whose lattice spacing has been rescaled by \( L \). The RG transformation is simply \( p' = R(p : L) \) where \( R(p : L) \) is the configurational weight of all spanning walks on the original cell and \( p' \) is the renormalized weight. The non-trivial fixed point of this recursion relation gives an estimate of \( \mu \), and the exponent \( v \) is given by \( v = \ln(L)/\ln(\lambda) \), where \( \lambda \) is the eigenvalue of the linearized RG transformation.

For SAW's on the simple cubic lattice, we use cells of size \( L^3 \) (see figure 1). For \( L = 2 \) and \( L = 3 \) we find the following recursion relations,

\[
p'(L = 2) = p^2 - 4 p^5 + 4 p^5 + 8 p^6 + 12 p^6 + 14 p^7 + 16 p^8 + 10 p^9, \tag{2}
\]

\[
p'(L = 3) = p^3 - 6 p^5 + 30 p^5 - 106 p^6 + 352 p^7 + 826 p^8 + 2378 p^9 + 5086 p^{10} + 13774 p^{11} + 26426 p^{12} + 67666 p^{13} + 116734 p^{14} + 278128 p^{15} + 409188 p^{16} + 878346 p^{17} + 1066878 p^{18} + 2013600 p^{19} + 1951424 p^{20} + 3133930 p^{21} + 2295390 p^{22} + 2962104 p^{23} + 1460748 p^{24} + 1369060 p^{25} + 340804 p^{26} + 170872 p^{27}. \tag{3}
\]

For \( L = 2 \) we find \( p^* = 0.297 3 \) with \( v = 0.587 5 \), and for \( L = 3 \), \( p^* = 0.275 5 \) with \( v = 0.581 4 \). Next we consider NAW's. Since, NAW's have not been considered previously by this method we first calculate \( v \) for NAW's on a square lattice. For the \( 2 \times 2 \) cell the recursion relation is \( p' = p^2 + 2 p^3 \). The fixed point of this recursion relation is at \( p^* = 0.5 \), and \( v = 0.756 5 \). We have calculated the recursion relation exactly for \( L \times L \) cells of size \( L \leq 5 \). The inverse slope of a plot of \( \ln(\lambda(L)) \) against \( \ln(L) \) gives an estimate of the true value of \( v \) [13]. In this way we find \( v \) to be about 0.758, compared to the Flory estimate [15] of 0.750. That the value of \( v \) in two dimensions is slightly larger than the Flory value has also been found for SAW's in field theory calculations [4], and in the large cell version of the present approach [12]. Our estimate agrees with the more accurate of these two estimates [12]. The critical fixed point value of \( p \) is equal to the reciprocal of the connectivity constant \( \mu \) [1,10]. Using finite size scaling theory arguments [13],

we have extrapolated our sequence of \( p^*(L) \) for \( L = 2 \) to 5 and we find \( p_\mu \) to be about 0.44 or \( \mu \sim 2.3 \). This value compares very well with the best series estimate [14] of \( \mu = 2.316 \pm 0.002 \).

We now consider NAW's in three dimensions. The recursion relations for \( L = 2 \) and \( L = 3 \) are,

\[
p'(L = 2) = p^2 - 4 p^3 + 6 p^4 + 4 p^5, \tag{4}
\]

\[
p'(L = 3) = p^3 - 6 p^4 + 26 p^5 + 84 p^6 + 230 p^7 + 655 p^8 + 900 p^9 + 1474 p^{10} + 2014 p^{11} + 2984 p^{12} + 378 p^{13} + 124 p^{15} + 12 p^{16}. \tag{5}
\]

Equations (4) and (5) have critical fixed points at \( p^* = 0.325 3 \) and at \( p^* = 0.301 1 \), respectively. The exponent \( v \) is 0.636 6 for \( L = 2 \) and 0.626 0 for \( L = 3 \). The best series estimate for \( \mu \) for NAW's on a simple cubic lattice is 4.046 ± 0.003 [14], and for SAW's on a simple cubic lattice \( \mu = 4.6838 \) [16]. We expect that the reciprocals of \( p^* \) 's to converge to these values in the large cell limit. The best experimental estimate [3] for \( v \) in three dimensions is 0.586 ± 0.004 and the best theoretical estimate [4] is 0.588 ± 0.001 5. Our results for \( v \) for the SAW's are particularly in good agreement with these estimates. However, our results for the NAW's are off by \( 7 \) %. This is not entirely unexpected because the extremely larger number of realizations for SAW's (18 562 857 on the \( 3^3 \) cell), compared to NAW's (only 6 238 on the \( 3^3 \) cell), should give a better value for \( v \).

To improve the estimates of \( v \) one must calculate the recursion relations for larger cells and then extra-
polate the results to \( L \to \infty \) [13]. Unfortunately, it is not feasible to calculate the recursion relations exactly for cubic cells with \( L > 3 \). This might prompt one to try to extrapolate our 2 point results to the \( L \to \infty \) limit. However, as it was pointed out previously [10], such two point extrapolations cannot be taken seriously. The best procedure will be to use a Monte Carlo technique [12, 13] for very large cells and then extrapolate the results to \( L \to \infty \).

3. Summary. — We have used a direct position space renormalization group approach [10] to calculate the polymer excluded volume exponent \( v \) in three dimensions without reference to the zero-component spin system [5]. Present calculations show that an obvious advantage of the direct approach as compared to those based on the magnetic analogy [4, 5, 6, 7], is its transparency and the relative ease with which calculations can be carried out. In this study, we restricted ourselves to cases where the recursion relations could be calculated exactly. This procedure has the advantage that the results are based on analytic rather than approximate calculations, but it also has the disadvantage that analytic calculations could only be carried out for small cells. To extend these results to larger cells one can use an approximate method, such as the Monte Carlo large cell approach [12, 13].

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