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LETTER TO THE EDITOR

Real-space renormalisation group approach for linear and branched polymers

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Abstract. A real-space renormalisation group (RG) approach for polymers is presented and is used to calculate the exponent ν for the radius of gyration of three types of molecules on a square lattice. In all three cases the excluded volume effect is taken into account. The three cases studied are linear polymers, randomly branched polymers without loops and randomly branched polymers in which branch end-points are allowed to join either to other branch ends or to polyfunctional units, thereby forming loops. We refer to the latter two configurations as *branched polymers* and *branched polymers with loops*, respectively. We find that ν decreases from its linear chain value as the concentration of polyfunctional units is increased and branched polymers are formed. However, ν is only slightly changed as loop fugacity is increased and branched polymers with loops are produced. Next, a new two-parameter RG is developed and it is found that linear polymers and branched polymers are described by two different fixed points, indicating that they belong to different universality classes. As the fugacity for loop formation is increased, the global flow diagram remains unchanged. This result supports the hypothesis that branched polymers with and without loops, in a good solvent, belong to the same universality class.

1. Introduction

Linear polymers are formed when a large number of bivalent monomers join to form a chain molecule. In the presence of a good solvent, repulsive monomer–monomer interactions lead to the excluded volume effect (Flory 1971), and statistics of long, isolated linear molecules are equivalent to self-avoiding walks (SAWs) on a lattice. With polyfunctional units, branched molecules can form, and the statistics of such polymer molecules are much more complex than those of the linear chain. Very recently, Redner (1979) has used Monte Carlo methods, and Lubensky and Isaacson (1979) have used field-theoretic RG techniques to study the statistics of branched polymers in a good solvent.

In this Letter, we present preliminary results of a real-space renormalisation group (RSRG) study of linear polymers and branched polymers. Previous direct applications of RSRG to polymers have been limited to the study of SAWs (Shapiro 1978, de Queiroz and Chaves 1979, Redner and Reynolds 1980, unpublished). However, using the techniques presented here, we study three types of molecular configurations in a good solvent where the excluded volume effect is present. We use a two-dimensional lattice model in which bifunctional monomers are represented by lattice bonds and polyfunctional branching units are represented by lattice sites. We calculate the exponent ν for the radius of gyration of linear polymers, randomly branched polymers without

loops and randomly branched polymers in which branch end-points are allowed to join either to other branch ends or to polyfunctional units, thereby forming a closed loop. Throughout this paper, we refer to the latter two molecular configurations as *branched polymers* and *branched polymers with loops*. In addition, we develop a two-parameter RG for polymers in which both the monomer fugacities and the concentration of polyfunctional units are renormalised. The model of branched polymers with loops presented here has the same statistics as random *bond* animals on a lattice (Lubensky and Isaacson 1979). Applications of the techniques presented here to the animal problem will be presented elsewhere (Family 1980, unpublished).

The outline of this Letter is as follows. The lattice model of polymers is defined in § 2. In § 3, we first outline the RSRG approach for polymers and then use it to study the three types of polymers mentioned above. In § 4, we present a two-parameter RG transformation for polymers. We discuss the results and give a brief summary in § 5.

2. The model

Consider a regular lattice of bonds and sites. If each bond is regarded as a monomer, a single connected cluster of n bonds is an isolated polymer molecule of size n . When polyfunctional units are introduced, they can occupy the sites and branches *may* form by the attachment of three or more monomers to these sites. We assume that the excluded volume constraint is present, and therefore a branch cannot intersect itself or another branch and only one monomer may join two neighbouring sites on the lattice. We use this model to study linear polymers, branched polymers and branched polymers with loops.

The basic function of interest is the number of polymers of size n , W_n . We define the generating function $W(p)$ as

$$W(p) = \sum_n W_n p^n. \quad (1)$$

The parameter p is the weight or fugacity associated with a monomer, so that a polymer of size n has a weight p^n . The mean-square radius of gyration $\langle R_n^2 \rangle$ and the mean-square end-to-end length ξ^2 are defined by

$$\langle R_n^2 \rangle = \sum_{i,r_i} r_i^2 W_n(r_i) / n \sum_{r_i} W_n(r_i) \quad (2)$$

and

$$\xi^2(p) = \sum_n \langle R_n^2 \rangle W_n p^n / \sum_n W_n p^n \quad (3)$$

where $W_n(r_i)$ is the number of polymers of size n with the i th site at a distance r_i from the centre of mass. The analogy of the above relations to counterparts in thermal phase transitions motivates the following definitions of polymer critical exponents. In the limit $n \rightarrow \infty$, we write

$$W_n \underset{n \rightarrow \infty}{\sim} \mu^n n^{-\theta}, \quad (4)$$

$$\langle R_n^2 \rangle^{1/2} \underset{n \rightarrow \infty}{\sim} n^\nu \quad (5)$$

and, as $p \rightarrow p_c$,

$$\xi(p) \underset{p \rightarrow p_c}{\sim} (p - p_c)^{-\nu}, \quad (6)$$

where $p_c = \mu^{-1}$. The connectivity constant μ is a lattice-dependent quantity that increases with increasing coordination number. On the basis of the universality hypothesis in phase transitions, we expect the exponents ν and θ to be universal and independent of the detailed form of the lattice chosen for the model. We will concentrate on the calculation of ν and p_c in this paper and will not discuss the exponent θ any further.

3. Real-space renormalisation group for polymers

The RG approach we use is a modified version of the RSRG developed for the percolation model by Reynolds *et al* (1977). The basic difference is that the parameter p for a polymer is a fugacity and not a probability. We first choose a lattice and partition it into cells that both cover the lattice and maintain its original symmetry. For the ease of calculations, we choose a square lattice and divide it into cells; one such cell is shown in figure 1. The RG transformation renormalises a polymer of size n (and weight p^n) to a single monomer of weight p' in the horizontal (vertical) direction if it 'gets across' the cell horizontally (vertically). In the cell shown in figure 1, we define getting across horizontally (vertically) as starting at 0 and ending at either point 1 or 2 (3 or 4). Other definitions of 'getting across' may be used, and it is expected that all acceptable rules converge to the same results in the large cell.

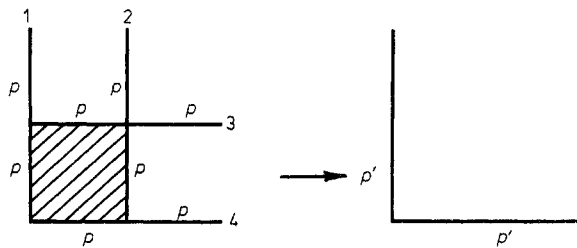


Figure 1. An example of the elementary cells used for polymer configurations on a square lattice. The case shown is a 2×2 cell. After renormalisation the cell becomes a horizontal (vertical) monomer if the polymer configuration spans horizontally (vertically).

We define an RG transformation by the sum of the configurational weights of all polymers which get across the cell. The non-trivial fixed point p^* (Wilson 1975) of this transformation gives an estimate of $p_c (= 1/\mu)$. The exponent ν is then given by

$$\nu = \ln(L)/\ln \lambda, \quad (7)$$

where λ is the eigenvalue of the linearised RG transformation about $p = p^*$, and L is the rescaling length.

Consider the 2×2 cell of figure 1. Here, $L = 2$ and there are 8 bonds on which monomers may be placed. If branching and loop formation are excluded, then the only

possible configurations are SAWS (or linear polymer chains), and the recursion relation for this case is

$$p' = p^2 + 2p^3 + p^4. \quad (8)$$

The non-trivial fixed point is at $p^* = 0.4656$ and $\nu = 0.7152$ (de Queiroz and Chaves 1979). If we introduce polyfunctional units, but still prohibit loop formation, then three or more monomers can branch out from a site and the resulting molecule will be a (tree-like) branched polymer. The recursion relation becomes

$$p' = p^2 + 4p^3 + 14p^4 + 22p^5 + 16p^6 + 4p^7. \quad (9)$$

The fixed point of this recursion relation is at $p^* = 0.2725$ and the exponent $\nu = 0.5760$. If we now allow the branch ends to join to other branch ends or to polyfunctional units and form loops, the number of possible configurations increases. The recursion relation becomes

$$p' = p^2 + 4p^3 + 14p^4 + 24p^5 + 21p^6 + 8p^7 + p^8. \quad (10)$$

Now, the fixed point is at $p^* = 0.2702$ and $\nu = 0.5712$.

In order to treat linear polymers and branched polymers with the same RG transformation, we introduce two new parameters into the model. We choose b to represent the probability that a randomly chosen site on a polymer is a polyfunctional unit, and we choose l , which we shall call the loop parameter, to represent the fugacity for the branch ends to join and form loops. When b and l are zero, only linear chains can occur. As b increases, but $l = 0$, tree-like branched polymers are produced. Finally, for non-zero values of l the end-points in the branched polymer may join together or to a branching unit to form loops. With these additional parameters, the three recursion relations (8), (9) and (10) can be combined into one general expression. The result is

$$p' = p^2 + p^3(2 + 2b) + p^4(1 + 12b + b^2) + p^5(10b + 12b^2 + 2b^2l) \\ + p^6(2b + 12b^2 + 2b^3 + b^2l + 4b^3l) + p^7(2b^2 + 2b^3 + 2b^3l + 2b^4l) + p^8b^4l. \quad (11)$$

Clearly, equation (11) reduces to equation (8) if both b and l are zero, while for $b = 1$, $l = 0$ it reduces to equation (9) and finally for $b = l = 1$ it reduces to equation (10).

Next, we study the 3×3 cell. This cell has 18 bonds on which monomers may be placed. The recursion relation has the form

$$p' = \sum_{n=1}^{18} \sum_{s=0}^9 \sum_{r=0}^4 c(s, r, n) b^s l^r p^n, \quad (12)$$

where s is the number of branch points, r is the number of closed loops, and n is the number of monomers. The coefficients $c(r, s, n)$ are too long to be reproduced here, but the results for ν and p^* obtained using equation (12) for the three cases of interest are shown in table 1, along with the values obtained for the 2×2 cell.

The result for the SAW exponent improves as the cell size increases. This is to be expected because, as the size of the cell increases, the corrections due to surface effects decrease. However, for cells of appreciable size, calculating the exact recursion relation is not possible. Thus, we must find other methods to obtain more accurate results.

One possibility is simply to extrapolate our two-point results to the $L \rightarrow \infty$ limit. Following equation (7), Reynolds *et al* (1978, 1980) have suggested that the sequence $\nu^{-1}(L)$ should be extrapolated against the variable $1/\ln(L)$. In the asymptotic limit ($L \rightarrow \infty$) the intercept should be the true eigenvalue. In this way we find ν (SAW) =

Table 1. The results for ν and p_c are listed for the three types of polymer configurations considered. Our best estimates are those obtained by the 'cell-to-cell' transformation technique ($L \rightarrow 1$) in which cells of size $L = 3$ are renormalised to cells of size $L = 2$.

	Polymer configuration	$L = 2$	$L = 3$	$L \rightarrow 1$
ν	Linear	0.7152	0.7187	0.7226
	Branched	0.5760	0.5986	0.6370
	Branched with loops	0.5712	0.5926	0.6273
$p_c = \mu^{-1}$	Linear	0.4656	0.4468	0.4319
	Branched	0.2725	0.2642	0.2577
	Branched with loops	0.2702	0.2609	0.2538

0.725, $\nu(\text{branched polymer}) = 0.641$ and $\nu(\text{branched polymer with loops}) = 0.633$. Indeed these numbers extrapolate in the right direction. However, we refrain from attaching much significance to this two-point extrapolation for two reasons. First, there are no theoretical arguments that show how the extrapolation ought to be carried out for small L . Second, Reynolds *et al* (1978, 1980) have found that there is a considerable curvature in extrapolation of the small-cell results. Therefore, extrapolation of small-size cells to the $L \rightarrow \infty$ limit is suspect on general grounds. Once large-cell RG techniques are used then the results can be extrapolated to the $L \rightarrow \infty$ limit.

One can also consider the opposite case: an 'infinitesimal transformation' in which $L \rightarrow 1$ (Reynolds *et al* 1978). In this limit the RG transformation should become exact. We first rescale a cell of linear dimension L to a monomer and obtain a transformation $R(L)$. Another cell, with linear dimension L' slightly smaller than L , has an analogous transformation $R(L')$. We use these two recursion relations to define implicitly a 'cell-to-cell' transformation from a cell of size L to a cell of size L' . This transformation rescales the length by L/L' . The value of p at which $R(L) = R(L')$ corresponds to p_c . The exponent ν is obtained from

$$\nu = \ln(L/L') / \{\ln[dR(L)] / \ln[dR(L')]\}_{p=p^*}, \quad (13)$$

where p^* is the fixed point value of p in the cell-to-cell transformation, and dR means dR/dp .

From equations (11) and (12) we calculate the recursion relation for the '3 × 3 to 2 × 2' transformation. The exponent ν and p_c are determined as a function of the branching probability and the loop parameter for the three cases of interest, and the results are listed in table 1. The result for ν is also shown in figure 2. This consists of two graphs put next to one another. The left-hand plot (*a*) shows the decrease in ν for a branched polymer as the concentration of polyfunctional units is increased (with $l = 0$). At the point $b = 0$ we obtain the SAW exponent for the linear chain. This value decreases as $b \rightarrow 1$. At $b = 1$ and $l = 0$ we have the first point of the right-hand plot (*b*), which shows the variation of ν for a branched polymer as loop parameter is increased. In this graph, we have drawn a straight line at the value of $\nu = 0.637$ to emphasise that there is a very small change in the value of ν as loop fugacity is increased from 0 to 1—a result which we had observed for all our small-cell calculations. If these results are any

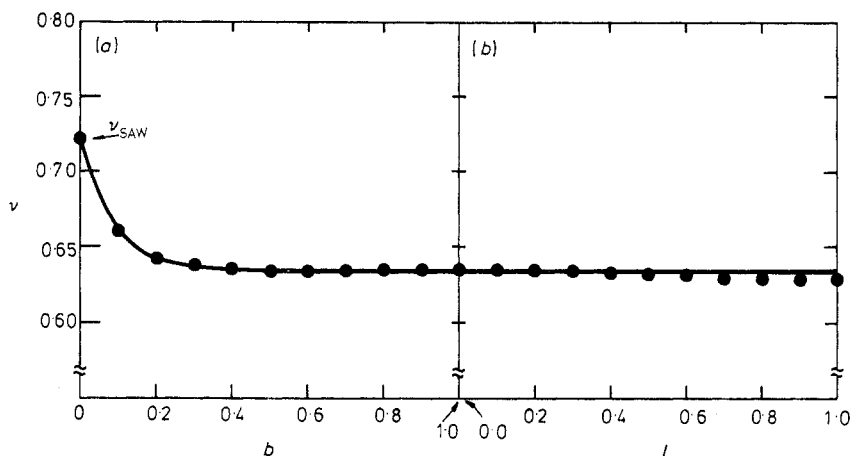


Figure 2. Dependence of ν on the concentration of polyfunctional units, b , and on the loop fugacity, l . The graph (a), for $l = 0$, shows ν against b when the molecular configurations are branched polymers without loops (tree graphs). The graph (b), for $b = 1$, shows the variation of ν for a branched polymer as the fugacity for loops (l) is increased. The data are the results of the 'cell-to-cell' transformation and the solid lines are guides to the eye. In (b) a straight line is drawn at the value of $\nu = 0.637$ to emphasise the small change in ν as l is increased.

indication of the true picture, they support the hypothesis (Lubensky and Isaacson 1979) that branched polymers with and without loops belong to the same universality class.

4. Two-parameter renormalisation group

Thus far, we have considered a one-parameter renormalisation group. In the generalised three-parameter recursion relations (11) and (12), b and l were included only as fixed, dependent parameters. A number of questions of interest, such as the nature of the crossover from the linear to branched polymers as b increases or whether the three types of polymers studied belong to the same universality class, cannot be answered by a one-parameter RG. As a first step in answering such questions, we consider a two-parameter RG transformation in which both the monomer weights and the branching probabilities are renormalised. However, we continue to treat l as a dependent variable.

Our recursion relation for the renormalised monomer weight (p') is simply equation (11), discussed previously. We define a scheme for renormalising the polyfunctional units as follows. A configuration of polyfunctional units on the original cell renormalises to a single branch point if the polymer configuration on the site part of the cell (the shaded region in figure 1) spans the cell either horizontally or vertically. This requires that a polymer start at 0 and be able to extend to either 1 or 2 or to 3 or 4. For example, in figure 3, we have shown a site configuration (figure 3(a)) which renormalises to a branch point and one which does not (figure 3(b)). These conditions define a recursion formula, giving b' , the renormalised branching probability, as a function of b . When all sites on a polymer are occupied by polyfunctional units ($b = 1$), all sites on

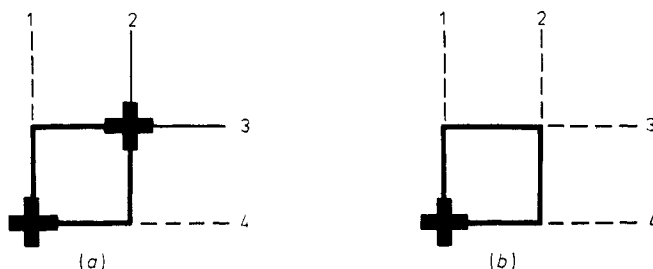


Figure 3. Renormalisation of polyfunctional units. A polymer configuration with polyfunctional units renormalises to b' if it can extend *either* to 1 or 2 *or* to 3 or 4. (a) Example of a configuration that renormalises to a polyfunctional unit. (b) Example of a configuration that cannot extend to either 1 or 2 *or* to 3 or 4. It does not renormalise to a polyfunctional unit.

the renormalised polymer must be occupied by branching units ($b' = 1$). To preserve a probabilistic interpretation of b and b' , we write b' as the sum of all branched polymers that renormalise according to the criterion we described above, divided by all possible configurations. The denominator will include all diagrams of the type shown in figure 3, whereas the numerator includes only the spanning configurations, such as the one shown in figure 3(a). In this way we find

$$b' = N/D, \quad (14)$$

where

$$\begin{aligned} N &= b(1-b)^3(4p+7p^2+10p^3) + b^2(1-b)^2(2p+8p^2+18p^3+3p^4l) \\ &\quad + b^3(1-b)(3p^2+14p^3+3p^4l) + b^4(4p^3+p^4l), \\ D &= 2p(1-b)^2 + p^2(2-b-b^2) + 2p^3(1+b) + p^4bl. \end{aligned}$$

The coupled recursion relations (11) and (14) together constitute a two-parameter RG transformation. When $b \rightarrow 0$, $b' \rightarrow 0$ and equation (11) reduces to equation (8). When $b \rightarrow 1$, $b' \rightarrow 1$ and equation (11) reduces to that for the branched polymer. Note that b' vanishes when $p \rightarrow 0$, indicating that there cannot be any polymer configuration with polyfunctional units alone.

Equations (11) and (14) may be solved numerically for the fixed points, critical surface and critical exponents. For $l = 0$ the global flow is shown in figure 4. There are two unstable fixed points at $(p^*, b^*) = (0.4656, 0.0)$ and $(0.2725, 1.0)$, corresponding to the SAW fixed point and the branched polymer fixed point, respectively. The direction of the flow is from the line of zero branching probability (i.e. linear polymers) to the branched polymer fixed point, indicating that *linear polymers and branched polymers belong to two different universality classes*. The branched polymer fixed point controls the flow away from the $b = 0$ axis. The critical surface is shown as the solid line in figure 4. It is obtained by following the flow trajectories from the SAW fixed point towards the branched polymer fixed point. Along this line the critical behaviour is that of the branched polymer.

Linearisation of the recursion relations (11) and (14) near the SAW fixed point ($p^* = 0.4656$, $b^* = 0$) gives $\lambda_1 = 2.636$ and $\lambda_2 = 2.802$ for the eigenvalues along the p and b axes, respectively. Since both eigenvalues are greater than unity, the SAW fixed point is unstable in both directions. The exponent ν (along the SAW line, ($b = 0$)) is

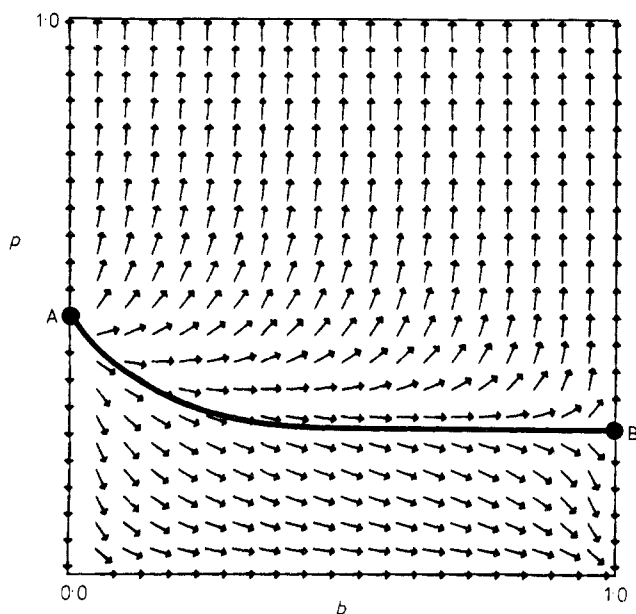


Figure 4. Global flow diagram from equations (11) and (14) with $l=0$. Each arrow indicates the local direction of flow. The critical surface is shown as the solid line. It connects the linear polymer (SAW) fixed point A (on the $b=0$ axis) to the branched polymer fixed point B (on the $b=1$ axis).

unchanged. The crossover exponent $\phi = \ln \lambda_2 / \ln \lambda_1 = 1.1$. This means that the critical curve leaves the SAW point tangentially to the p axis.

By linearising the recursion relations near the branched polymer fixed point ($p^* = 0.2725$, $b^* = 1$), we find only one non-zero eigenvalue, $\lambda = 3.331$. Thus, only one eigenvalue is relevant and the two-parameter group does not change the critical exponents of the branched polymer, but demonstrates that the SAWs and branched polymers belong to two different universality classes.

The above discussion was limited to the case $l=0$, but we find that as l changes from 0 to 1 the global picture of the flow vectors remains unchanged. There is only a slight change in the position of the fixed point at $b=1$, but no new fixed point is found. Thus, we are led to believe that branched polymers with and without loops belong to the same universality class, as suggested by Lubensky and Isaacson (1979).

5. Discussion and summary

We now turn to a discussion of our numerical estimates of ν and p_c , shown in table 1. Our best estimates are those obtained using the 'infinitesimal transformation' ($L \rightarrow 1$). For two-dimensional linear polymers, the best estimate for ν is 0.75 and for $p_c (= 1/\mu)$ on a square lattice is about 0.38 (McKenzie 1976), which is consistent with our preliminary results. For branched polymers in a *good solvent*, we know only of the works of Redner (1979), and of Lubensky and Isaacson (1979).

Redner (1979) has used Monte Carlo techniques to study the mean end-to-end distance of branched polymers and branched polymers in which branch end-points are

allowed to join and form loops. He finds the same value of ν for both branched polymers and branched polymers with loops—this conclusion is consistent with our result that loops are not important for branched polymers in a good solvent. However, the statistics of Redner's branched polymers are different from those discussed here, and his exponent need not have the same value as our estimate.

Lubensky and Isaacson (1979) have used a field-theory RG technique to study the model of branched polymers discussed here. In an ϵ expansion about $\epsilon = 8 - d$, they calculate the critical exponents. Unfortunately, since $\epsilon = 6$ when $d = 2$, their results for the exponents cannot be useful numerically in two dimensions. However, Lubensky and Isaacson point out that the generating function defined by equation (1) is equivalent to the generating function for the number of random animals on a lattice. Thus, the exponent ν for a branched polymer with loops is equivalent to the exponent ρ defined by Stauffer (1979) for the mean radius of gyration of a random animal. Monte Carlo results for two-dimensional *site* random animal radii predict ν to be about 0.65 to 0.66 (Stauffer 1979). If site and bond animals belong to the same universality class, then ν should be the same for bond animals and branched polymers with loops, which is consistent with our estimates.

The lattice connectivity constant μ has been calculated for the *bond* animals in the study of d -dimensional percolation processes (Gaunt and Ruskin 1978). The best estimate for μ (called λ in the animal literature) for bond clusters on a square lattice gives p_c of about 0.2 for branched polymers with loops, again consistent with our preliminary estimates.

In summary, we have presented a real-space renormalisation group approach for polymers that can be applied to both linear and branched polymer configurations. Whenever comparison is possible, our numerical results are consistent with the available estimates. In addition, we have developed a two-parameter RG transformation, and have found that linear polymers and branched polymers are described by two different fixed points, and therefore belong to two different universality classes. As the loop fugacity is increased, the global flow diagram and the critical exponents remain essentially unchanged. This result supports the hypothesis that branched polymers with and without loops belong to the same universality class (Lubensky and Isaacson 1979).

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