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Polymers with Annealed and Quenched Branchings Belong to Different Universality Classes

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ABSTRACT: We show with the help of simple Flory-type arguments that critical indices ν for the swelling of a branched polymer with a quenched system of branchings and with annealed branchings differ so that $\nu_{\mathrm{qu}} < \nu_{\mathrm{ann}}$. This is due to the fact that the process of rearranging branchings accompanies swelling of the annealed polymer. This difference becomes drastic in some physical manifestations, e.g., behavior in capillaries. We also discuss briefly the behavior of annealed polymers in the regime of a semidilute solution.

I. Introduction

Randomly branched polymers are of significant interest both for synthetic polymer chemistry and for biophysics. For instance, RNA molecules with secondary structure are branched. Two types of branched polymers exist: quenched and annealed. In quenched branched polymers the positions of branching points are fixed. On the other hand, in annealed branched polymers the positions of branch points fluctuate and are in thermal equilibrium with the other conformational degrees of freedom. In previous analytical works[1-6] and numerical simulations[7,8] annealed branching was assumed (sometimes not explicitly).

We will show that polymers with quenched and annealed branchings belong to different universality classes (at least above the Θ-point) and will give a Flory-type estimate of corresponding critical indices. We shall discuss properties of treelike molecules without internal cycles—as was assumed in other papers.[1-8]

The physical reason for the difference between quenched and annealed branching is the following. Introduction of excluded volume leads to stretching of subchains in the case of quenched branching but for annealed branching it is accompanied by rearrangement of branchings. This leads to an extra contribution to the corresponding entropy and, as we shall show, changes the universality class of the problem. This fact (changed structure of branchings) was noticed in recent numerical work.[8]

II. Calculation of Swelling Exponents of Branched Polymers

Consider the free energy of a branched polymer of N monomers with characteristic end-to-end distance R. In a Flory-type approximation

$$F = F_{\mathrm{el}}(R) + \frac{vN^2}{R^d} \tag{1}$$

where $F_{\mathrm{el}}(R)$ is the elastic free energy and v is the excluded volume. This expression was used in refs 3 and 4 with F_{el} taken in complete analogy with the Flory-type derivation for linear polymers:

$$F_{\mathrm{el}}(R) = T\frac{R^2}{{R_0}^2} \tag{2}$$

with $R_0 \sim lN^{1/4}$, which represents the unperturbed size of a polymer having Kuhn segment l. From eqs 1 and 2 the result

$$R \sim N^{5/[2(d+2)]} \tag{3}$$

was obtained.[3,4] However, this result is applicable for quenched but not annealed polymers because in its derivation only elastic entropy (2) of Gaussian subchains was taken into account and rearrangement of branchings which takes place in annealed polymers was ignored.

To take into account this rearrangement, one should notice that the characteristic number of bonds ("length of a path") from one end to the other in an unperturbed polymer is $\sim N^{1/2}$. (From this fact the average distance between two ends is $\sim N^{1/4}$ for the ideal polymer.[1]) This is, however, not necessarily true for a polymer with excluded volume and an annealed system of branchings. Under the influence of stretching, branchings will also move and change the characteristic number of bonds between ends.

To take this factor into account, we have to estimate the corresponding entropy of stretching. To do this, we will use the diagrammatic recursive method suggested in ref 2 in the simplest version of the model where only ends and branchings are allowed (no bifunctional units or linear parts). The results can be easily generalized to a case which includes linear insertions.

To estimate the entropy, we have to calculate $G(L,N)$, the partition function of a branched polymer of N monomers with the L bonds between two arbitrary fixed ends. The diagrammatic expression for $G(L,N)$ is given in Figure 1. The corresponding equation for $G(L,N)$ is

$$G(L,N) = \sum_{l_1,\ldots,l_L} Z(l_1)Z(l_2)\ldots Z(l_L)\delta(l_1+\ldots+l_L+2-N) \tag{4}$$

where $Z(l) = \sum_L G(L,l)$ is the complete partition function of the polymer. This was calculated in ref 2 with the result (in terms of our simplified model with only ends and branching without linear insertions) $Z(l) = 2^l/l^{3/2}$. $G(L,N)$ can be obtained from eq 4 by the technique of Laplace transform. As a result we obtain

$$S_{\mathrm{br}} = \ln G(L,N) = -\frac{L^2}{N} \tag{5}$$

for the entropy associated with the structure of branchings.

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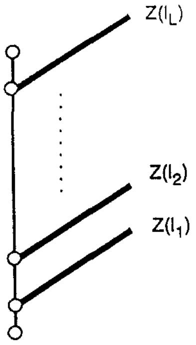

Figure 1. A diagram corresponding to $G(L,N)$. Thick lines denote the partition function of a branched polymer of l_s monomers. There are a total of L such insertions. Thin lines are propagators corresponding, in this model, to individual chemical bonds.

The free energy of a polymer with annealed branchings has the form

$$F_{\mathrm{ann}} = \frac{vN^2}{R^d} + T\frac{R^2}{L} + T\frac{L^2}{N} \tag{6}$$

This is to be minimized with respect to L and R. Minimization with respect to L gives the new critical index ρ defined by the equation $L \sim N^{\rho}$ with

$$\rho = \frac{d+6}{3d+4} \tag{7}$$

For the total entropy of an annealed polymer which includes entropy associated with the change of branchings we obtain

$$S_{\mathrm{ann}} = R^{4/3}/N^{1/3} \tag{8}$$

From this by minimization with respect to R we obtain $R \sim N^{\nu_{\mathrm{ann}}}$, with

$$\nu_{\mathrm{ann}} = 7/(3d+4) \tag{9}$$

This is the central result of this work. As can be seen, index $\nu_{\mathrm{ann}} = 1/4$ (unperturbed) at the critical dimension $d_c = 8$, in accord with earlier results.[3] It is worth noting that our result for annealed polymers coincides with the result obtained for quenched polymers at $d = d_c$. This is not surprising as at $d = 8$, $\rho = 1/2$, which means that the effect of rearranging branchings which determines the main difference between the quenched and annealed cases disappears. Also at $d = 1$ we have $R \sim N$, which is reasonable because in one dimension polymers with excluded volume must be linear and completely stretched. For $d = 3$, $\nu_{\mathrm{ann}} = 7/13$, which is slightly larger than $\nu_{\mathrm{qu}} = 1/2$. However, we must note here that the result for quenched branchings obtained in ref 3 with the help of Flory-type estimates coincides with the exact result for annealed branchings obtained in ref 5 by field-theoretic methods. We can consider this as a coincidence in three-dimensional space. For instance, in one dimension the estimate for the quenched case gives $\nu_{\mathrm{qu}}(d=1) = 5/6$ which seems to be a less realistic estimate than our $\nu_{\mathrm{ann}}(d=1) = 1$.

III. Comparison with Simulation Results and Possible Experimental Implications

It is interesting to compare these Flory-type estimates for annealed branched polymers with estimates for quenched polymers[4] and with numerical results from Monte Carlo simulations[8] (Tables I and II). Numerical values for ν_{ann} and ν_{qu} are rather close to each other at $d = 3$. Also at $d = 3$ ν_{qu} obtained from Flory theory[4] coincides with the exact result for annealed polymers ($\nu_{\mathrm{ann}} = 0.5$ at $d = 3$) obtained by the field-theoretic approach in ref 5. By continuation this will be true for nearby dimensions 2 and 4, with the estimate for ν_{qu} fitting numerical results for annealed polymers slightly better than the estimate for ν_{ann}. However, from our estimates and, more important, from the fact that branches are able to rearrange in annealed polymers, we obtain the inequality that $\nu_{\mathrm{ann}} \geq \nu_{\mathrm{qu}}$. Another interesting relation $\rho = (2\nu + 1)/3$ between the indices ρ and ν_{ann} follows from our estimates. We compared this result with numerical experiment (Figure 2).[8] There are only three points available (corresponding to the cases $d = 2$, $d = 3$, and $d = 4$) but at least from these three points we see good agreement between simulations and theoretical estimates.

Table I
Comparison of the Present Results with the Results[4] for Index ν for a Quenched Polymer and Data from Numerical Experiments[8]

	d							
	1	2	3	4	5	6	7	8
annealed[a]	1.0	0.7	0.538	0.438	0.368	0.318	0.28	0.25
quenched[b]	0.833	0.625	0.5	0.417	0.357	0.313	0.278	0.25
		0.637	0.496 (0.5)[c]	0.420				

[a] $\nu = 7/(3d + 4)$. [b] $\nu = 5/[2(d + 2)]$. [c] Exact result from ref 5.

Table II
Comparison of This Work's Estimate of the Index ρ with the Results of Numerical Simulations[8]

	d				
	1	2	3	4	8
theory[a]	1.0	0.8	0.692	0.625	0.5
numerical results[8]		0.737	0.652	0.608	

[a] $\rho = (d + 6)/(3d + 4)$.

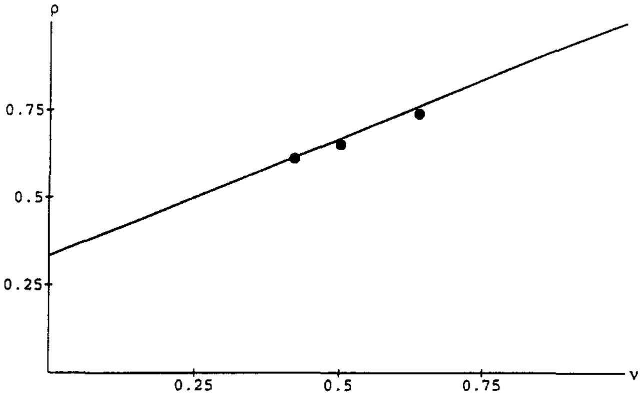

Figure 2. Plot of $\rho(\nu)$. Solid line is the result of the present work: $\rho = (2\nu + 1)/3$. Dots are results of numerical experiments at $d = 2$, $d = 3$, and $d = 4$ obtained in ref 8.

An annealed branched polymer is slightly more stretched than a quenched branched polymer. To illustrate the implication of this difference, we may consider a simple example of a branched polymer in a capillary of diameter D. First consider the quenched case (Figure 3a). This will have size $R_0 \sim N^{1/2}$ in the direction along the capillary and will be compressed to D in the two other directions. The free energy of a polymer is assumed to have a scaling form:

$$\Delta F_{\mathrm{qu}} \sim T\phi(D/R_0) \sim T\phi(D/lN^{1/2}) \tag{10}$$

with power law asymptotics of the function $\phi(x) \sim x^{\alpha}$. To determine the exponent α, we note that the pressure on capillary walls $p = \partial\Delta F/R_0\partial D^2$ must not depend on polymer length but depends only on concentration N/D^2R_0 of

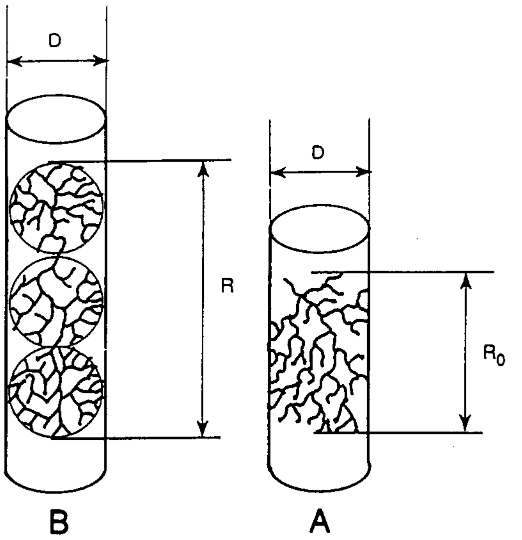

Figure 3. Branched polymer in a capillary: (A) quenched; (B) annealed. Spheres in B denote blobs.

monomers. This condition gives $\alpha = 4$ and finally

$$\Delta F_{\mathrm{qu}} = N^2\frac{l^4}{D^4} \tag{11}$$

We now consider the case of annealed branchings. In this case the size of a polymer along the capillary will not necessarily be equal to R_0. Due to reconfiguration of the system of branchings, the length of a polymer along the direction of a capillary must be proportional to N. We may use a presentation of a polymer as set of blobs each of g monomers (Figure 3B). The number of blobs is N/g and the free energy is[9] $\Delta F_{\mathrm{ann}} = TN/g$. We have to determine the number of monomers g in a blob. This can be easily done from the condition that the size of a blob equals the size of a capillary D. Using eq 9, we obtain $lg^{7/(3d+4)} \sim D$ and the free energy is

$$\Delta F_{\mathrm{ann}} = N\left(\frac{l}{D}\right)^{(3d+4)/7} \tag{12}$$

At $d = 3$ this gives

$$\Delta F_{\mathrm{ann}} = N\left(\frac{l}{D}\right)^{13/7}$$

These simple estimates show the difference in behavior of branched polymers with a quenched and with an annealed system of branchings. This difference is especially striking in the example of a branched polymer in a capillary. In fact, our estimates show that the thinnest capillary penetrable for a quenched polymer has the size $D^0_{\mathrm{qu}} \sim lN^{1/4}$ (at $D = D_0$, $\Delta F_{\mathrm{qu}} \sim N$) and at smaller diameters of a capillary, the free energy grows drastically. For annealed polymers the thinnest capillary has width $D^0_{\mathrm{ann}} \sim l \ll D^0_{\mathrm{qu}}$. This result may have some biological implications as it shows a drastic difference in the penetrability of membrane channels by RNA with unstable secondary structure (annealed case) and RNA with rigid fixed secondary structure (quenched case).

Another example of the difference between quenched and annealed branched polymers concerns their behavior in semidilute solution. The scaling relation for the osmotic pressure is given by

$$\Pi = \frac{c}{N}\left(\frac{c}{c^*}\right)^x$$

where $c^* = N/R_0{}^d$ is the threshold concentration for the crossover between dilute and semidilute solutions.[9] The exponent x is determined from the condition that the osmotic pressure does not depend on the polymer length N in the semidilute regime.[9] This gives $\Pi \sim c^\delta$, with $\delta = 3$ for quenched polymers and $\delta = 21/8$ (at $d = 3$) for annealed polymers.

We have shown that quenched and annealed polymers exhibit different behavior, and these differences can be observed in numerical simulations or experiments. We hope that this work will stimulate such experiments.

Our consideration is based on simple Flory-type arguments. There are more rigorous field-theoretic approaches for description of annealed branched polymers.[10,11] We think that these approaches can be modified using the replica method to describe the quenched case. However, in both cases the critical dimension $d_c = 8$, and therefore $\epsilon = 8 - d$ expansion is not very realistic for practical situations.

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