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Critical behavior of randomly branched polymers with quenched branchings

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Randomly branched polymers with quenched branchings, in which monomers interact with each other through the excluded volume interaction, are investigated by using an approach of conformation-space renormalization group theory combined with the replica technique. The perturbation expansion for the mean-square radius of gyration is found and the scaling variable is identified. The renormalization group analysis shows that the critical exponents of the radius of gyration ($\nu=1/4+\epsilon/40$) and of the total number of configurations ($\theta=5/2-3\epsilon/20$) no longer obey the scaling law $\theta-1=(D-2)\nu$, where $\epsilon=8-D$ and D is the space dimensionality, which is tenable for randomly branched polymers with *annealed* branchings.

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I. INTRODUCTION

The theoretical description of the conformational properties of randomly branched polymers (RBP's) is an interesting subject due to its obvious applications in synthetic physical chemistry and biology for investigating problems of gels, proteins, and nucleic acids [1]. In a recent paper, based on a Flory-type argument, Gutin, Grosberg, and Shakhnovich [2] demonstrated that annealed and quenched RBP's do not belong to the same universality class due to the difference in the branching structures. The principal difference between quenched and annealed RBP's is that the introduction of the excluded volume does not change the branching structure of quenched RBP's, while it does affect the branching structure of annealed RBP's. The matter has been further studied by Monte Carlo simulations [3].

For annealed RBP's, there have been intensive theoretical [1] and computer-simulational [4] investigations for several decades. Several approaches of statistical mechanics have been suggested to deal with the problem of the conformational properties [5–8]. It was shown that the problem of annealed RBP's can be mapped to other areas of statistical mechanics, such as lattice animals [7] and Ising magnetic systems [8]. A recent conformation-space field theory of annealed RBP's [9] provided further understanding of the essential universal characteristics of annealed RBP solutions when the excluded volume interaction is present. The mean-square radius of gyration and the total number of configurations of RBP's having contour length L grow as L^{ν} and $L^{-\theta}b^{L}$ for large L, respectively, where ν and θ are the universal gyration and configuration exponents, and b is a nonuniversal constant. It was also established that the gyration exponent has the value $\nu=0.5$ for $D=3$, and the gyration and configuration exponents obey the scaling relation [8]

$$\theta-1=(D-2)\nu , \tag{1.1}$$

where D is the space dimensionality. The field-theory ϵ expansions for these exponents $\nu=\frac{1}{4}+\epsilon/36$ and $\theta=\frac{5}{2}-\epsilon/12$ agree with this relation [7,9]. Equation (1.1) was obtained [8] for D-dimensional animals by relating to the Lee-Yang edge singularity of the Ising model in an imaginary magnetic field in $(D-2)$ dimensions.

In contrast, much less is known about quenched RBP's [10]. The Flory-type argument yielded, for example, a gyration exponent ν smaller than that of annealed RBP's [2]. The off-lattice Monte Carlo simulations of RBP's [3] supported this argument and yielded the values ν (quenched)$=0.45\pm0.01$ and ν (annealed)$=0.49\pm0.01$. In this paper, we apply the approach of conformation-space renormalization group theory [9] to study analytically a model of quenched RBP's interacting through the excluded volume interaction. We focus, in particular, on the scaling behaviors of the mean-square radius of gyration and of the configuration number. We obtain the ϵ expansions for the gyration exponent $\nu=\frac{1}{4}+\epsilon/40$ and the configuration exponent $\theta=\frac{5}{2}-3\epsilon/20$, which are found no longer to obey the scaling relation mentioned above for annealed RBP's.

The replica approach [11] has been shown to be a powerful tool for analyzing quenched random systems, including random heteropolymers, random copolymers, and random cross-linked macromolecules. Here we implement the replica technique to deal with the quenched branching structures in the calculation of the mean-square radius of gyration to first order in the excluded volume. The monomers interact with each other through the excluded volume interaction characterized by the excluded volume parameter u_0. The fact that the monomer-monomer interaction itself is *not* random makes the calculation of the replica theory possible: all we need to do is to generalize our previous formalism [9]

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to a higher dimensional space. Gutin, Grosberg, and Shakhnovich [12] also discussed the formalism of a RBP model based on the replica approach, in which monomers interact with each other through random interactions, a situation more closely resembling the RNA secondary structures [10]. Such a case is not discussed here.

The paper is organized as follows. In Sec. II the microscopic model is described. In Sec. III, asymptotic expansions in powers of the excluded volume for the partition function, the mean-square radius of gyration, and the second virial coefficient are calculated by using the t'Hooft-Veltman dimensional regularization scheme [13]. The results are used to evaluate the exponents of the mean-square radius of gyration and of the total number of configurations based on the conformation-space renormalization group scheme. In Sec. IV a discussion is given.

II. MODEL

The model system consists of branched polymers composed of trifunctional units only, which may grow one (end), two (linear connection), or three branches. Consider a treelike branched polymer of total contour length L and Kuhn length l, moving in a D-dimensional hyperspace of volume V. The polymer is assumed to have $2n+1$ linear portions separated by two tribranching points, or a tribranching point and an end. We use κ, where $\kappa=1,2,\ldots,2n+1$, to label these linear portions. Our main assumption is that the noninteracting statistical weight factor of the κth linear portion, of length L_κ, obeys the D-dimensional Gaussian distribution [14]

$$g_\kappa(D,[\mathbf{r}])=\frac{1}{(4\pi)^{D/2}}\exp\left[-\frac{1}{4}\int_0^{L_\kappa}dt_\kappa\left|\frac{d\mathbf{r}(t_\kappa)}{dt_\kappa}\right|^2\right]. \tag{2.1}$$

For convenience, here we use the rescaled variable $\mathbf{r}(t_\kappa)$, which is related to the position of the κth chain, $\mathbf{x}(t_\kappa)$, as a function of the contour variable t_κ, by $\mathbf{r}(t_\kappa)\equiv(2D/l)^{1/2}\mathbf{x}(t_\kappa)$. The statistical distribution function can then be written

$$G_B(D,[\mathbf{r}])=\prod_{\kappa=1}^{2n+1}g_\kappa(D,[\mathbf{r}])\exp(-v[\mathbf{r}])\ , \tag{2.2}$$

where the subscript B denotes the fact that the distribution function $G_B(D,[\mathbf{r}])$ explicitly depends on the branching structure of the molecule, and $v[\mathbf{r}]$ represents the excluded volume interaction potential

$$v[\mathbf{r}]=\tfrac{1}{2}u_0\sum_{\kappa=1}^{2n+1}\sum_{\kappa'=1}^{2n+1}\int_0^{L_\kappa}dt_\kappa\int_0^{L_{\kappa'}}dt'_{\kappa'}\delta[\mathbf{r}(t_\kappa)-\mathbf{r}(t'_{\kappa'})]\ . \tag{2.3}$$

The magnitude of the interaction is represented by u_0, the bare, i.e., unrenormalized, excluded volume parameter. Note that it is implicitly assumed that the integral in Eq. (2.3) is constrained so that the contour distance between the two considered contour points is greater than a cutoff length, which has the magnitude of the Kuhn length [15]. The restriction eliminates self interactions of monomer units, which would otherwise appear as dimensional singularities in the theory [16,9].

For quenched branched polymers, the topology of the branching structure is fixed while all of the possible configurations included in Eq. (2.2) are accessible to the polymers. We assume that the method of preparing the branching structures places the branching points *at random,* so that all different branching structures may occur. We further assume that the branching structures are prepared by the chemical process with a fixed activity Λ^2, and that the excluded volume interaction $v[\mathbf{r}]$ is not present during the process. In this model, the probability to find a given structure B with n tribranching points is given by

$$P_B=\frac{\Lambda^{2n}}{Q_0}\ , \tag{2.4}$$

where Q_0 is the partition function of noninteracting RBP's,

$$Q_0=\int\mathcal{D}[\mathbf{r}]\sum_B\Lambda^{2n}g_B(D,[\mathbf{r}])\ , \tag{2.5}$$

where $\sum_B$ denotes the summation over all possible branching structures. In Eq. (2.5), we also have

$$g_B(D,[\mathbf{r}])=\prod_{\kappa=1}^{2n+1}g_\kappa(D,[\mathbf{r}])\ . \tag{2.6}$$

The explicit form of Q_0 can be found by using the approach developed by de Gennes [6,9],

$$Q_0=\frac{I_1(2\Lambda L)}{\Lambda L}\ , \tag{2.7}$$

where $I_1(x)$ is the first-order modified Bessel function of the first kind.

To understand the consequence of a similar model for annealed RBP's at the mean-field level when $v[\mathbf{r}]=0$, de Gennes [6] considered an approach that simultaneously samples the phase space of the branching structure and the configuration freedom associated with Eq. (2.5). We can show that at the mean-field level, the model described above for quenched RBP's gives the same results.

Taking the dimension of the contour length L as the fundamental dimension λ of the theory, $[L]=\lambda$, one can [9] deduce $[\mathbf{r}]=\lambda^{1/2}$, $[u_0]=\lambda^{D/2-2}$, $[\Lambda]=\lambda^{-1}$, $[L/\Lambda]=\lambda^2$, and $[u_0\Lambda^2]=\lambda^{-\epsilon/2}$, where

$$\epsilon=D_c-D=8-D\ . \tag{2.8}$$

We may show that the upper critical dimensionality D_c equals 8 by a similar discussion as in Appendix C of Ref. [9], where the correlation function $G(\mathbf{k})$ is now calculated by invoking the replica technique. The dimensional singularities that show up as powers of $1/\epsilon$ when the cutoff length is taken to be zero may be extracted by the approach of the dimensional regularization scheme, and treated by the minimum subtraction renormalization method [13]. The calculation in this paper will follow these procedures.

III. CALCULATIONS

A. Partition function

The overall number of configurations of quenched RBP's is related to the partition function

$$Q=\sum_B P_B Q_B \ , \tag{3.1}$$

where Q_B is the partition function for a given branching structure B:

$$Q_B=\langle 1\rangle_B \ . \tag{3.2}$$

Here and hereafter we use the notation

$$\langle f[\mathbf{r}]\rangle_B=\int \mathcal{D}[\mathbf{r}]G_B(L,[\mathbf{r}])f[\mathbf{r}] \ , \tag{3.3}$$

to denote the average value of a physical quantity $f[\mathbf{r}]$ for a given branching structure. Combining Eqs. (3.1) and (3.3), one finds that the partition function Q has exactly the same form as that obtained for annealed RBP's. At large L, we have [9]

$$\frac{Q}{Q_0}=1+\frac{2u_0\Lambda^2}{(4\pi)^4\epsilon}\left[\frac{16\pi^2 L}{\Lambda}\right]^{\epsilon/4}(1+0.105\epsilon)+O(u_0^2) \ . \tag{3.4}$$

B. Mean-square radius of gyration

The mean-square radius of gyration of quenched RBP's is given by

$$\overline{S^2}=\sum_B P_B(\overline{S^2})_B \ , \tag{3.5}$$

where $(\overline{S^2})_B$ is the mean-square radius of gyration for a given branching structure B, which can be evaluated through the coherent-scattering structure factor $\mathcal{S}_B(\mathbf{k})$ [9]:

$$(\overline{S^2})_B=-\frac{l}{2}\left.\frac{\sum_{i=1}^{D}\partial^2\mathcal{S}_B(\mathbf{k})/\partial k_i^2}{\mathcal{S}_B(\mathbf{k})}\right|_{\mathbf{k}=0} \ , \tag{3.6}$$

where $\mathcal{S}_B(\mathbf{k})$ is defined as

$$\mathcal{S}_B(\mathbf{k})=\sum_{\kappa,\kappa'}\int_0^{L_\kappa}dt_\kappa\int_0^{L_{\kappa'}}dt'_{\kappa'}\langle \tfrac{1}{2}\exp[i\mathbf{k}\cdot[\mathbf{r}(t_\kappa)-\mathbf{r}(t'_{\kappa'})]]\rangle_B \ . \tag{3.7}$$

Noting that $\partial\mathcal{S}_B(\mathbf{k},L)/\partial k_i|_{\mathbf{k}=0}=0$, from Eqs. (3.5) and (3.7) we rewrite Eq. (3.6) as

$$\overline{S^2}=-\frac{l}{L^2}\sum_{i=1}^{D}\frac{\partial^2}{\partial k_i^2}\sum_{\kappa,\kappa'}\int_0^{L_\kappa}dt_\kappa\int_0^{L_{\kappa'}}dt'_{\kappa'}\sum_B P_B\ln\langle \tfrac{1}{2}\exp[i\mathbf{k}\cdot[\mathbf{r}(t_\kappa)-\mathbf{r}(t'_{\kappa'})]]\rangle\bigg|_{\mathbf{k}=0} \ . \tag{3.8}$$

To evaluate the average over the branching probability P_B shown in Eq. (3.8), we use the replica technique [11]

$$\sum_B P_B\ln f_B=\lim_{m\to 0}\sum_B P_B\frac{(f_B)^m-1}{m} \ . \tag{3.9}$$

The use of Eq. (3.9) in Eq. (3.8) yields

$$\overline{S^2}=-\frac{l}{mL^2}\sum_{i=1}^{D}\frac{\partial^2}{\partial k_i^2}\mathcal{S}_R(m,\mathbf{k})\bigg|_{\mathbf{k}=0,m=0} \ , \tag{3.10}$$

where $\mathcal{S}_R(m,\mathbf{k})$ can be regarded as the coherent-scattering factor of the m-replica system

$$\mathcal{S}_R(m,\mathbf{k})=\tfrac{1}{2}\sum_{\kappa,\kappa'}\int_0^{L_\kappa}dt_\kappa\int_0^{L_{\kappa'}}dt'_{\kappa'}\int\prod_{\alpha=1}^{m}\mathcal{D}[\mathbf{r}^\alpha]\sum_B P_B\prod_{\alpha=1}^{m}G_B(D,[\mathbf{r}^\alpha])\exp\left[i\sum_{\alpha=1}^{m}\mathbf{k}\cdot[\mathbf{r}^\alpha(t_\kappa)-\mathbf{r}^\alpha(t'_{\kappa'})]\right] \ , \tag{3.11}$$

where the last integration is to be conducted over the coordinates of all m mutually noninteracting replicas, $\{\mathbf{r}^\alpha\}$. Introducing the mD-dimensional coordinate $\mathbf{R}=\{\mathbf{r}^1,\mathbf{r}^2,\ldots,\mathbf{r}^m\}$ and momentum $\mathbf{K}=\{\mathbf{k},\mathbf{k},\ldots,\mathbf{k}\}$, one may rewrite Eq. (3.11) as

$$\mathcal{S}_R(m,\mathbf{k})=\tfrac{1}{2}\sum_{\kappa,\kappa'}\int_0^{L_\kappa}dt_\kappa\int_0^{L_{\kappa'}}dt'_{\kappa'}\int\mathcal{D}[\mathbf{R}]\sum_B P_B g_B(mD,[\mathbf{R}])\exp\left[-\sum_\alpha v[\mathbf{r}^\alpha]\right]\exp(i\mathbf{K}\cdot[\mathbf{R}(t_k)-\mathbf{R}(t'_{\kappa'})]) \ . \tag{3.12}$$

Equation (3.12) has basically the same form as the one we encountered in calculating the mean-square radius of gyration of annealed RBP's, except that here we need to consider the mD-dimensional instead of D-dimensional physical quantities.

We are interested in a series expansion in terms of powers of u_0. It is straightforward to extend the formula for the correlation functions given in Ref. [9] to the mD-dimensional description (see the Appendix). To first order in u_0 we have

$$\mathcal{S}_R(m,\mathbf{k})=\frac{1}{2!0!Q_0}\mathcal{L}_L^{-1}G_2(0,0;\mathbf{K},-\mathbf{K};p)$$

$$-\frac{u_0}{(2!)^2Q_0}\mathcal{L}_L^{-1}\int\frac{d^{(mD)}\mathbf{Q}}{(2\pi)^{(mD)}}G_4(0,0;\mathbf{K},-\mathbf{K},\mathbf{Q},-\mathbf{Q};p)\sum_{\alpha=1}^{m}\left[\prod_{\beta\neq\alpha}\delta(\mathbf{Q}^{\beta})\right]+O(u_0^2)\ , \tag{3.13}$$

where $\mathcal{L}_L^{-1}$ denotes the inverse Laplace transformation, and $\delta(\mathbf{q})$ is the Kronecker delta function. The functions G_2 and G_4 are the correlation functions of the m-replica system, with two and four internal monomer positions being specified, whose expressions can be found in the Appendix. The calculation of $\mathcal{S}_R(m,\mathbf{k})$ is tedious but straightforward. We use the dimensional regularization scheme to extract the singularities appearing in $\mathcal{S}_R(m,\mathbf{k})$. Inserting the obtained $\mathcal{S}_R(m,\mathbf{k})$ into Eq. (3.10) yields the asymptotic behavior at large L:

$$\overline{S^2}=\frac{lD}{2}\left[\frac{\pi L}{\Lambda}\right]^{1/2}\left[1+\frac{2u_0\Lambda^2}{3(4\pi)^4\epsilon}\left[\frac{16\pi^2L}{\Lambda}\right]^{\epsilon/4}(1-0.303\epsilon)\right]+O(u_0^2)\ . \tag{3.14}$$

This result differs from $\overline{S^2}$ obtained for annealed RBP's [9].

C. Second virial coefficient

We assume that the interaction $v[\mathbf{r}_1,\mathbf{r}_2]$ between the two considered branched polymers is given by

$$v[\mathbf{r}_1,\mathbf{r}_2]=u_0\sum_{\kappa_1=1}^{2n_1+1}\sum_{\kappa_2'=1}^{2n_2+1}\int_0^{L_{\kappa_1}}dt_{\kappa_1}\int_0^{L_{\kappa_2'}}dt'_{\kappa_2'}\delta[\mathbf{r}_1(t_{\kappa_1})-\mathbf{r}_2(t'_{\kappa_2'})]\ . \tag{3.15}$$

The second virial coefficient A_2, averaged over all possible branching structures, can be expressed as

$$A_2=\sum_{B_1}P_{B_1}\sum_{B_2}P_{B_2}(A_2)_{B_1B_2}\ , \tag{3.16}$$

where $(A_2)_{B_1B_2}$ is the structure-dependent second virial coefficient when polymer 1 has structure B_1 containing n_1 branchings, and polymer 2 has structure B_2 containing n_2 branchings [9]:

$$(A_2)_{B_1B_2}=\frac{\int\mathcal{D}[\mathbf{r}_1]g_{B_1}(D,[\mathbf{r}_1])\exp(-v[\mathbf{r}_1])\int\mathcal{D}[\mathbf{r}_2]g_{B_2}(D,[\mathbf{r}_2])\exp(-v[\mathbf{r}_2])1-\exp\{-v[\mathbf{r}_1,\mathbf{r}_2]\}}{\int\mathcal{D}[\mathbf{r}_1]g_{B_1}(D,[\mathbf{r}_1])\exp(-v[\mathbf{r}_1])\int\mathcal{D}[\mathbf{r}_2]g_{B_2}(D,[\mathbf{r}_2])\exp(-v[\mathbf{r}_2])}\ . \tag{3.17}$$

To second order in u_0, Eq. (3.17) gives

$$(A_2)_{B_1B_2}=\int\mathcal{D}[\mathbf{r}_1]g_{B_1}(D,[\mathbf{r}_1])\int\mathcal{D}[\mathbf{r}_2]g_{B_2}(D,[\mathbf{r}_2])v[\mathbf{r}_1,\mathbf{r}_2]\left[1+\int\mathcal{D}[\mathbf{r}_1]g_{B_1}(D,[\mathbf{r}_1])v[\mathbf{r}_1]+\int\mathcal{D}[\mathbf{r}_2]g_{B_2}(D,[\mathbf{r}_2])v[\mathbf{r}_2]\right]$$

$$-\int\mathcal{D}[\mathbf{r}_1]g_{B_1}(D,[\mathbf{r}_1])\int\mathcal{D}[\mathbf{r}_2]g_{B_2}(D,[\mathbf{r}_2])v[\mathbf{r}_1,\mathbf{r}_2][v[\mathbf{r}_1]+v[\mathbf{r}_2]+\tfrac{1}{2}v[\mathbf{r}_1,\mathbf{r}_2]]+O(u_0^3)\ . \tag{3.18}$$

Noting that

$$\int\mathcal{D}[\mathbf{r}_1]g_{B_1}(D,[\mathbf{r}_1])\int\mathcal{D}[\mathbf{r}_2]g_{B_2}(D,[\mathbf{r}_2])=1 \tag{3.19}$$

and

$$\int\mathcal{D}[\mathbf{r}_1]g_{B_1}(D,[\mathbf{r}_1])\int\mathcal{D}[\mathbf{r}_2]g_{B_2}(D,[\mathbf{r}_2])v[\mathbf{r}_1,\mathbf{r}_2]=u_0L^2\ , \tag{3.20}$$

one can easily verify that, to the second order in u_0, A_2 has the same form as the one obtained for annealed RBP's. At large L, we have [9]

$$A_2=u_0L^2\left\{1-\frac{2u_0\Lambda^2}{3(4\pi)^4\epsilon}\left[\frac{16\pi^2L}{\Lambda}\right]^{\epsilon/4}[1+O(\epsilon)]\right\}+O(u_0^3)\ . \tag{3.21}$$

However, the three-loop contribution to A_2, which is not considered in the present calculation, is different from its counterpart of annealed RBP's.

D. Renormalization group calculation

The singularities $1/\epsilon$ in Eqs. (3.4), (3.14), and (3.21) can be removed by introducing the renormalization constants Z_u, Z_M, and Z, which connect the renormalized quantities u_r, M_r, and F_r to the bared ones $u=u_0\Lambda^2\lambda^{\epsilon/2}/(4\pi)^4$, $M=L/\Lambda$, and $F=Q/Q_0$ through [9]

$$u_r=Z_u^{-1}u\ , \tag{3.22}$$

$$M_r=Z_MM\ , \tag{3.23}$$

and

$$F_r=Z^{-1}F\ , \tag{3.24}$$

where the normalization coefficients Z_M, Z_u, and Z are assumed to be functions of u_r.

To first order in u_r, using Eqs. (3.4), (3.14), and (3.21), we obtain

$$Z_u = 1 + \frac{10u_r}{3\epsilon} + O(u_r^2) \ , \tag{3.25}$$

$$Z_M = 1 + \frac{4u_r}{3\epsilon} + O(u_r^2) \ , \tag{3.26}$$

and

$$Z = 1 + \frac{2u_r}{\epsilon} + O(u_r^2) \ . \tag{3.27}$$

The renormalization function $\beta(u_r) = \partial u_r / \partial \ln\lambda$ used to determine the fixed point u_r^* is then calculated to be

$$\beta(u_r) = \tfrac{1}{2}\epsilon u_r - \tfrac{5}{3}u_r^2 + O(u_r^3) \ . \tag{3.28}$$

Letting $\beta(u_r^*) = 0$ yields the fixed point

$$u_r^* = \frac{3\epsilon}{10} + O(\epsilon^2) \ . \tag{3.29}$$

Using Eqs. (3.22), (3.23) and (3.25), (3.26) in Eq. (3.14) and then replacing u_r by u_r^*, we find

$$\overline{S^2} = \frac{lD}{2}(\pi M_r)^{1/2} \left[\frac{16\pi^2 M_r}{\lambda^2} \right]^{\epsilon/20} (1 - 0.060\epsilon) \ , \tag{3.30}$$

and

$$\frac{Q}{Q_0} = \left[\frac{16\pi^2 M_r}{\lambda^2} \right]^{3\epsilon/20} (1 + 0.063\epsilon) \ . \tag{3.31}$$

According to Eqs. (3.30) and (3.31), the critical exponents ν and θ defined by $\overline{S^2} \sim L^{2\nu}$ and $Q \sim L^{1-\theta} b^L$, where b is a nonuniversal constant, are thus given to first order in ϵ by

$$\nu = \frac{1}{4} + \frac{\epsilon}{40} + O(\epsilon^2) \tag{3.32}$$

and

$$\theta = \frac{5}{2} - \frac{3\epsilon}{20} + O(\epsilon^2) \ . \tag{3.33}$$

IV. DISCUSSION

The gyration exponent ν of quenched RBP's in Eq. (3.32) is smaller than that of the annealed RBP's ν (annealed)$= \frac{1}{4} + \epsilon/36$ [7,9]. It is difficult to estimate the actual value of the exponent at $D=3$ based on the one-term ϵ expansion (3.32). Monte Carlo simulations indicate that, at $D=3$, we have ν (quenched) ≈ 0.45 [3] and ν (annealed) ≈ 0.50 [4]. It is generally believed that the latter agrees with the predicted value ν (annealed)$=0.5$ [8]. For a comparison, the Flory-type argument yields ν (quenched) ≈ 0.5 and ν (annealed) ≈ 0.538 [2], which shows a similar *relative* difference between the two exponents compared to the result obtained by the Monte Carlo calculations [3].

The exponent θ in Eq. (3.33) is also different from its counterpart in annealed RBP's, θ (annealed)$= \frac{5}{2} - \epsilon/12$. Up to order ϵ, the renormalization group theories [7,9] for annealed RBP's yield exponents ν and θ, satisfying the scaling relation in Eq. (1.1), which is a general equation predicted by Parisi and Sourlas for any ϵ [8]. Such a scaling relation is no longer tenable for the present quenched model. Furthermore, it is doubtful whether or not the connections between the problem of RBP's and the Lee-Yang edge singularity of the Ising magnetic model, as studied by Parisi and Sourlas [8], still exist in the case of quenched RBP's.

While the exponents are different, the scaling behaviors of the two types of polymers are similar. The perturbation expressions for Q, $\overline{S^2}$, and A_2 [Eqs. (3.4), (3.14), and (3.21)] show that a scaling parameter z defined by

$$z = \frac{u_0 \Lambda^2}{(4\pi)^4} \left[\frac{16\pi^2 L}{\Lambda} \right]^{\epsilon/4} \tag{4.1}$$

is naturally produced. The same form of the scaling parameter has also been found earlier for the problem of annealed RBP's [9]. Generalizing the perturbation result, we propose a closed asymptotic formula for the mean-square radius of gyration at large L,

$$\overline{S^2} \sim \left[\frac{L}{\Lambda} \right]^{1/2} z^{2(4\nu-1)/\epsilon} \ . \tag{4.2}$$

This asymptotic behavior has been checked by using the results of Monte Carlo simulations [3]. To make a proper comparison with Eq. (4.2) we rescaled the off-lattice Monte Carlo simulation data of $\overline{S^2}$, in which the excluded volume parameter u_0 may vary, according to the z parameter defined in Eq. (4.1), and found that Eq. (4.2) is indeed satisfied at large L. We further note that the Flory-type argument is known to produce gyration exponents close to the actual values, despite the crudity of the approximations made to estimate the contributions to the free energy from the entropy and the interaction [17]. Even more surprising is the fact that it also naturally produces the appropriate form for the scaling parameter z for both linear [17] and branched [18,19,2,3] polymers.

In this paper, the conformational properties of quenched RBP's are obtained based on the model that describes the quenched branching structures produced by the chemical process without the presence of the excluded volume interaction. We do not claim, however, that other types of quenching distributions would also lead to the same result. Depending on *how* the structures are produced and quenched, the conformational properties may show different behaviors.

In summary, by using the perturbation approach of conformation-space field theory, we obtained first-order corrections to the mean-field behaviors of the partition function Q, the mean-square radius of gyration $\overline{S^2}$, and the second virial coefficient A_2 of quenched RBP's, in asymptotic expansions in powers of the excluded volume u_0. We have also deduced first-order terms in the ϵ expansions for the critical exponents ν and θ. Perturbation theory provides a direct verification of the following physical properties: (a) the mean-square radius of gyration follows the scaling behavior in Eq. (4.2) for large L; (b) quenched RBP's are more condensed than annealed RBP's; and (c) the scaling law [Eq. (1.1)] is not valid for quenched RBP's, while it is suitable for describing annealed RBP's.

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APPENDIX: CORRELATION FUNCTIONS FOR THE m-REPLICA SYSTEM

For the m replicas of noninteracting RBP's the probability of finding any two external ends being specified by the m-replica spatial coordinates $\mathbf{R}_1=\{\mathbf{r}_1^1,\mathbf{r}_1^2,\ldots,\mathbf{r}_1^m\}$ and $\mathbf{R}_2=\{\mathbf{r}_2^1,\mathbf{r}_2^2,\ldots,\mathbf{r}_2^m\}$ is

$$G_0(\mathbf{R}_1,\mathbf{R}_2;L)=\sum_B P_B\int_{\mathbf{R}_2}^{\mathbf{R}_1}\mathcal{D}[\mathbf{R}]g_B(mD,[\mathbf{R}]) \ . \quad \text{(A1)}$$

Introducing the Fourier and Laplace transformations

$$G_0(\mathbf{K};p)=\int\frac{d^{(mD)}\mathbf{K}}{(2\pi)^{(mD)}}\exp[i\mathbf{K}\cdot(\mathbf{R}-\mathbf{R}')]\times\int_0^\infty dL\,\exp(-pL)G_0(\mathbf{R},\mathbf{R}';L) \ , \quad \text{(A2)}$$

we obtain

$$G_0(\mathbf{K};p)=\frac{1}{\mathbf{K}^2+G_0^{-1}(p)} \ , \quad \text{(A3)}$$

where $\mathbf{K}=\{\mathbf{k}^1,\mathbf{k}^2,\ldots,\mathbf{k}^m\}$ is the mD-dimensional vector, and [6]

$$G_0(p)=\frac{2}{p+(p^2-4\Lambda^2)^{1/2}} \ . \quad \text{(A4)}$$

When the l internal points are specified by the mD-dimensional vectors $\mathbf{R}_1,\mathbf{R}_2,\ldots,\mathbf{R}_l$, and the two external ends are specified by the mD-dimensional vectors $\mathbf{R}$ and $\mathbf{R}'$, the correlation functions $G_l(\mathbf{R},\mathbf{R}';\mathbf{R}_1,\mathbf{R}_2,\ldots,\mathbf{R}_l;L)$, $l=1,2,\ldots$, for m-replicated RBP's can be introduced in the same way as in Ref. [9]. In the following, we list G_2 and G_4 in the Fourier-Laplace space, which is used in the text for the calculation of $\overline{S^2}$:

$$G_2(0,0;\mathbf{K},-\mathbf{K};p)=2G_0^2(p)G_0(\mathbf{K};p)Y(0;p)Y^2(\mathbf{K};p) \quad \text{(A5)}$$

and

$$\begin{aligned}G_4(0,0;\mathbf{K},-\mathbf{K},\mathbf{Q},-\mathbf{Q};p)={}&2G_0^2(p)Y(0;p)Y^2(\mathbf{K};p)Y^2(\mathbf{Q};p)\\&\times\{2G_0(p)G_0(\mathbf{K};p)G_0(\mathbf{Q};p)Y(0;p)[Y(K;p)Z^2(\mathbf{K};p)+Y(\mathbf{Q};p)Z^2(\mathbf{Q};p)+2\Lambda^2G_0^2(p)Y(0;p)]\\&+Z(\mathbf{K};p)Z(\mathbf{Q};p)[G_0(\mathbf{K};p)+G_0(\mathbf{Q};p)][G_0(\mathbf{K};p)Y(\mathbf{K};p)+G_0(\mathbf{Q};p)Y(\mathbf{Q};p)]\\&\times[G_0(\mathbf{K}+\mathbf{Q};p)Y(\mathbf{K}+\mathbf{Q};p)+G_0(\mathbf{K}-\mathbf{Q};p)Y(\mathbf{K}-\mathbf{Q};p)]+\Lambda^2G_0(p)[G_0(\mathbf{K};p)+G(\mathbf{Q};p)]^2\\&\times[G_0^2(\mathbf{K}+\mathbf{Q};p)Y^2(\mathbf{K}+\mathbf{Q};p)+G_0^2(\mathbf{K}-\mathbf{Q};p)Y^2(\mathbf{K}-\mathbf{Q};p)]\} \ ,\end{aligned} \quad \text{(A6)}$$

where

$$Y(\mathbf{K};p)=[1-\Lambda^2G_0(p)G_0(\mathbf{K};p)]^{-1} \quad \text{(A7)}$$

and

$$Z(\mathbf{K};p)=1+\Lambda^2G_0(p)G_0(\mathbf{K};p) \ . \quad \text{(A8)}$$

[1] For a review, see, e.g., M. Daoud and A. Lapp, J. Phys. Condens. Matter **2**, 4021 (1990), and references therein.

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