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Crossover between Gaussian and self-avoiding limits via finite order self-avoiding walk: Conformation space renormalization for polymers. VII

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The crossover between the random walk and the self-avoiding walk via finite order self-avoiding random walk (FSAW) is studied analytically with the aid of conformation space renormalization group theory. Explicit expressions for the end-vector distribution function and $\langle R^2 \rangle$ are given up to order $\epsilon = 4 - d$ (d the spatial dimension). Since the excluded volume parameter for FSAW is contour length dependent, it is very awkward to study the present crossover behavior by using the polymer–magnet analogy. In contrast, our calculations in conformation space are simple and transparent, showing the power of this RG approach. The crossover behavior along FSAW is compared with the crossover obtained when the magnitude of the excluded volume interaction is decreased. The crossover via FSAW may occur in situations where a very long single chain is immersed in a solution of (shorter) chains and the concentration of the (shorter) chains is increased.

I. INTRODUCTION

The self-avoiding walk (SAW) is widely accepted as a good model of a polymer chain in dilute solution with a good solvent.[1] The ordinary simple random walk (RW), on the other hand, is considered to be an acceptable model of a polymer chain in a dilute solution at the Flory (theta) temperature[2] and also in a sufficiently concentrated solution or in a melt.[2,3] SAW and RW are the two extreme models of long flexible polymer chains in solution. Therefore, the study of the crossover behavior between these two models is not only experimentally but also theoretically (and conceptually) important.

The crossover between SAW and RW generally occurs when the effective strength of the repulsive intrachain interactions changes. Conceptually, there can be two very different routes (or pathways) from SAW to RW. One route, the magnitude route M, is due to the decrease of the magnitude of the excluded volume parameter. The other route, the range route R, is due to the shrinkage of the *contour range* (note that this is not the actual spatial range of the interaction) of the excluded volume interaction.

Route M is a good model of the crossover behavior from the high temperature, good solvent limit to the θ point, and has been studied extensively.[4,5] For example,[5] closed form interpolation formulas for the end-vector distribution function, the mean-square end-to-end distance, the coherent scattering function, etc. have been given with semiquantitative agreement with experimental results.

The study of the route R is exactly that of the finite order self-avoiding walk (FSAW) considered by Domb and Hioe[6] and by Wall *et al.*[7] as an intermediate model to study SAW. In this model, an arbitrary monomer fixed in the chain is assumed to interact only with monomers *within* some prescribed "distance" M from the monomer *along* the chain i.e., interaction is present only within the prescribed contour distance M. If M is equal to the total length N of the polymer chain, then the chain is self-avoiding. If $M=0$, then the chain is a mere random walk chain. For $0 < M < N$, the chain is called[7] a FSAW of order M.

The naive blob argument of the French school[3,8] also reminds us of FSAW. In the blob argument, the crossover behavior from dilute solutions to semidilute solutions is explained by allowing a monomer to interact only with other monomers of the same blob because of the screening of intrachain interactions by density correlations. The restriction thus imposed on the allowed intrachain interactions is, therefore, more stringent than the FSAW. However, this apparently is because of a technical reason and the true spirit of the blob argument is better realized by FSAW. Since the blob argument is often utilized, it is important to know the detailed properties of the corresponding model, i.e., FSAW. In the dilute limit, the chain is in a single blob, so there is full excluded-volume interaction. In the semidilute regime, however, the chain is divided into many blobs of size ξ, the monomer–monomer correlation length. Hence, according to the blob picture, the chain should be modeled as a FSAW of order $\approx \xi^{1/\nu}$, (ξ must be supplied by other means, e.g., experiments) where ν is the exponent for the end-to-end distance. Since ξ can be measured experimentally, and the properties of a single test chain immersed in the semidilute solution can also be experimentally accessible, e.g., by suitable isotopic labeling, a knowledge of the properties of FSAW can be useful to test "blob picture." A detailed calculation of the end-vector distribution function[9] of a single test chain immersed in a semidilute solution shows that the function is somewhat different from that for the FSAW (of order $\xi^{1/\nu}$) presented here. This has also been suggested by the Monte Carlo calcula-

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tion of Walls and Seitz.[10] However, as is discussed in the end of the paper, the coarse grained properties such as the mean-square end-to-end distance $\langle R^2 \rangle$ of a test chain in the semidilute solution can be well mimicked by the FSAW of order $\xi^{1/\nu}$.

The focus of the present paper is, however, on the study of the route R itself and not on the situations which can be successfully modeled by the route R. The comparison of a single test chain behavior along route R and the true dilute–semidilute crossover will be given in a forthcoming paper.

To the best of our knowledge, there has been no systematic, analytic study of the FSAW end-vector distribution function. The main purpose of the present paper is to give a renormalization group theoretic calculation of the end-vector distribution function for a long FSAW chain as a function of θ, where $\theta = M/N$, the relative order of the FSAW. In the $\theta \to 0$ limit with fixed N, the chain behaves like a simple random walk and in the opposite $\theta \to 1$ limit with fixed N, it is like SAW. Although the renormalization group technique requires $M = N\theta$ to be much larger than the monomer size, sufficiently large N allows the study of the cases with very small θ. We can also study the asymptotic behavior of the chain in the $N \to \infty$ limit with θ fixed. Since the order $M = N\theta$ is not finite in this case, the chain is *not* Markovian. We shall see later that, in this limit, the end-to-end distance $\langle R^2 \rangle$ scales exactly as the full SAW. If M is fixed, then in the $N \to \infty$ limit, $\langle R^2 \rangle$ scales, of course, exactly as the simple RW.

Our calculation is of the ϵ expansion type, where $\epsilon = 4 - d$, d being the spatial dimensionality. Our past experience[11–14] has shown that this method is semiquantitatively reliable.

In the present problem, the coupling constant is contour length dependent, since there is no excluded volume interaction between two monomers further apart than the length $M < N$ along the chain. Hence, it is awkward to translate the FSAW problem into the field theoretic or magnetic language. Consequently, the polymer magnet analogy[15] is not useful to the present problem. The study of route R is a good example to exhibit the elegance and power of the conformation space renormalization method developed in the previous papers[11–14] of the present series.

In Sec. II, the model for route R is introduced and a short account of the calculational method is given. The results of the bare perturbation and their renormalization are given in Sec. III. Section IV gives final results and discussion, and the last section is a summary.

II. MODEL AND GENERAL CONSIDERATION ON THE CALCULATIONAL SCHEME

A. "Miscroscopic" model

The finite order self-avoiding walk (FSAW) of order M_0 and of length N_0 ($> M_0$) is a random walk chain of length N_0 each monomer (or unit) of which has excluded volume interactions only with other monomers within the contour distance M_0 from it. The contour length from a monomer is measured along the chain in which it is embedded. The dimensionless model Hamiltonian for the FSAW is given by

$$H_a(\mathbf{c}) = \frac{1}{2}\int_0^{N_0} \dot{\mathbf{c}}^2 \, d\tau + \tfrac{1}{2} v_0 \int_{N_0 \geq \tau \geq 0} d\tau \int_{\substack{M_0 \geq |\tau - \tau'| \geq a \\ N_0 \geq \tau' \geq 0}} d\tau' \; \delta(\mathbf{c}(\tau) - \mathbf{c}(\tau')) \,, \quad (2.1)$$

where $\mathbf{c}(\tau)$ represents the continuous chain spatial location (= the conformation of the chain) parametrized by the contour length $\tau \in [0, N_0]$, $v_0 (> 0)$ is the bare coupling constant (= excluded volume parameter), $\dot{\mathbf{c}} = d\mathbf{c}/d\tau$, and a is a cutoff contour length for the purpose of eliminating self-excluded volume interaction of (monomer) units. Note that the ratio $\theta \equiv M_0/N_0$ is the fundamental parameter describing the crossover: $\theta = 1$ is the SAW limit and $\theta = 0$ the RW limit.

As is clearly seen from the Hamiltonian (2.1), the excluded volume parameter is actually contour-length dependent, since for $|\tau - \tau'| > M_0$ the coupling term in Eq. (2.1) vanishes. It is explicitly shown in Ref. 16 that the polymer–magnet analogy is simple only when the interaction term can be written as a simple functional of the monomer density field

$$\rho(\mathbf{r}) = \int_0^{N_0} \delta(\mathbf{c}(\tau) - \mathbf{r}) \, d\tau \,.$$

For example, in the case of $\theta = 1$ (SAW), the interaction term is $v_0 \int \rho^2(\mathbf{r}) \, d\mathbf{r}/2$. Due to the one-to-one correspondence $\phi^2(\mathbf{r}) \leftrightarrow \rho(\mathbf{r})$ in the averaging procedure over the ensemble of all conformations, where ϕ is the spin density in the magnetic language,[16] the interaction term can be translated into a $\int (\phi^2)^2 \, d\mathbf{r}$ type self-interaction term. In the present case, however, there is no such simple expression for the interaction term. It is, therefore, awkward to use the polymer–magnet analogy or spin-dimension zero field theory[15] to calculate physical quantities related to the FSAW. In general, the field theoretic approach or grand canonical ensemble (with respect to the chain length) approach is of little use when the problem necessitates explicit occurrence of the contour variable. A good example, clearly illustrating this point, is the distribution function of the vector connecting two arbitrary fixed points on the chain.[17,14]

If C designates the (engineering) dimension of the contour length, then the dimensions of all quantities appearing in Eq. (2.1) are automatically determined because of the dimensionless character of H. The dimensions of Q are written as $[Q]$ and Eq. (2.1) implies

$$[\mathbf{c}] = C^{1/2}, \quad [a] = [N_0] = [M_0] = C, \quad [v_0] = C^{-\epsilon/2} \,,$$

where $\epsilon = 4 - d$, d being the spatial dimensionality.

B. Renormalization

The procedure adopted in the previous papers, especially paper III[11] and paper IV[12] of the present series, is closely followed in this paper. The bare distribution function for the end-to-end vector $\mathbf{R}$ depends on the cutoff length a, the total contour length N_0, the bare excluded volume parameter v_0, the relative order θ of FSAW and $\mathbf{R}$. On the other hand, macroscopic distribution function depends on the macroscopic length scale L, the macroscopic polymer size N, the excluded-volume

parameter v, R, and θ. For convenience, we use the coupling parameters in their dimensionless forms $u_0 = v_0 L^{\epsilon/2}$ and $u = vL^{\epsilon/2}$.

Since both N and N_0 must be proportional to the molecular weight, they are proportional to each other, and we write

$$N = Z_2 N_0 , \tag{2.2}$$

where Z_2 is independent of N. This implies that like the $u - u_0$ relation, Z_2 also is determined by the local property of the chain. We consider only the case $M_0 \gg a$, so that the relation between M and M_0 is given by $M = Z_2 M_0$. That is, as will be checked later, θ is not renormalized. The microscopically calculated unnormalized distribution function G_0 must be proportional to the macroscopically observable distribution function G so that

$$G = Z^{-1} G_0 . \tag{2.3}$$

The u-u_0 relation, Eq. (2.2), and Eq. (2.3) are formally fixed by the requirement that the macroscopic distribution function must remain well defined in the $a \to 0$ limit.

The procedure used repeatedly in the previous papers[11,12,5] yields the renormalization group equation for G,

$$\left[L \frac{\partial}{\partial L} + \beta(u) \frac{\partial}{\partial u} + \gamma_1(u) + \gamma_2(u) N \frac{\partial}{\partial N} \right] G(N, \mathrm{R}, \theta; u, L) = 0 , \tag{2.4}$$

where

$$\beta(u) = L(\partial u / \partial L)_{\theta, v_0, N_0, a \to 0} ,$$

$$\gamma_1(u) = L(\partial \ln Z / \partial L)_{\theta, v_0, N_0, a \to 0} ,$$

$$\gamma_2(u) = L(\partial \ln Z_2 / \partial L)_{\theta, v_0, N_0, a \to 0} . \tag{2.5}$$

This equation governs the functional form of G. The macroscopically observable G must satisfy Eq. (2.4) in the $a/L \to 0$ limit. Since we are interested in the intrachain interaction with full self-avoiding strength, we consider Eq. (2.4) only at the self-avoiding fixed point $u = u^* (> 0)$ with $\beta(u^*) = 0$,

$$\left(L \frac{\partial}{\partial L} + A + BN \frac{\partial}{\partial N} \right) G(N, \mathrm{R}, \theta; u^*; L) = 0 , \tag{2.6}$$

where $A = \gamma_1(u^*)$ and $B = \gamma_2(u^*)$. The numbers A and B can be identified with the conventional exponents as[11]

$$B = 1 - 1/2\nu, \quad A = (\gamma - 1)/2\nu .$$

From Eq. (2.6), the functional form of G is determined as

$$G(N, \mathrm{R}, \theta) = N^{\gamma - \nu d - 1} f(\mathrm{R}/N^{\nu}, \theta) , \tag{2.7}$$

where u^* and L are suppressed in the right-hand side.

III. CALCULATION OF G AND $\langle R^2 \rangle$

A. End-vector distribution

The unnormalized bare end-vector distribution function G_B can be obtained from the following formula:

$$G_B(N_0, \mathrm{R}, \theta; v_0, a) = \int_{\mathbf{c}(0)=0}^{\mathbf{c}(N_0)=\mathbf{R}} \mathfrak{D}[\mathbf{c}] \exp[-H_a(\mathbf{c})] , \tag{3.1}$$

where $\mathfrak{D}$ is the uniform measure on the conformation set. The perturbation expansion for G_B is given by a slight modification of the well-known series for the self-avoiding walk as

$$G_B(N_0, \mathrm{R}, \theta; v_0, a) = G_0(N_0, \mathrm{R}) - v_0 \int_0^{N_0 \theta} dx \int_0^{N_0 - x} d\tau \int d\mathbf{r} \times G_0(N_0 - x - \tau, \mathrm{R} - \mathbf{r}) G_0(x, 0) G_0(\tau, \mathbf{r}) + O(v_0^2) , \tag{3.2}$$

where G_0 is the unperturbed Gaussian distribution function

$$G_0(x, \mathbf{r}) = (2\pi x)^{-d/2} \exp(-\mathbf{r}^2/2x) \tag{3.3}$$

and the $a \to 0$ limit is taken. Equation (3.2) is calculated in $(4 - \epsilon)$ space, and can be written as

$$G_B(N_0, \mathrm{R}, \theta; v_0, a) = G_0(N_0, \mathrm{R}) - u_0 L^{\epsilon/2} I(\theta) \tag{3.4}$$

with

$$I(\theta) = \int_0^{N_0 \theta} dx (N_0 - x) G_0(N_0 - x, \mathrm{R}) G_0(x, 0) . \tag{3.5}$$

$I(1)$ is the quantity I of Eq. (4.3) in paper III,[11] so $I(\theta)$ can be calculated analogously as

$$I(\theta) = (2\pi)^{-d} N_0^{2-d} e^{-\alpha_0} G_\theta(\alpha_0) , \tag{3.6}$$

with

$$G_\theta(\alpha_0) = \frac{2}{\epsilon}(1 - \alpha_0) - \zeta^{-1} e^{-\alpha_0 \zeta} - 2 + 2 + (\alpha_0 - 1)(\hat{\gamma} + \ln \alpha_0) - \alpha_0 + (1 - \alpha_0) Ei(-\alpha_0 \zeta) + O(\epsilon) , \tag{3.6a}$$

where $\alpha_0 = R^2/2N_0$, $\zeta = \theta/(1 - \theta)$, $\hat{\gamma} \simeq 0.5772$ is Euler's constant, and $Ei(-x) = -\int_x^\infty dt \exp(-t)/t$. $G_1(\alpha_0)$ is $G(\alpha_0)$ given in Eq. (4.12) of paper III.[11] As is expected in the previous section, the singular term in Eq. (3.6a) is θ independent, so that Z and Z_2 are exactly the same as we have obtained in paper III[11]:

$$Z = 1 + u/2\pi^2 \epsilon + O(u^2) ,$$

$$Z_2 = 1 + u/2\pi^2 \epsilon + O(u^2) . \tag{3.7}$$

These results can also be checked easily by following the procedure given in paper III. Since the u-u_0 relation is determined by the local property of the chain, the result of paper III can be used in the present case also.

$$u_0 = u + 2u^2/\epsilon\pi^2 + O(u^3) . \tag{3.8}$$

It is clear that there is no need to renormalize θ.

After rewriting the bare perturbation series (3.4) in terms of N, M, and u, the renormalized perturbation series is obtained as

$$G(N, \mathrm{R}, \theta; u) = (2\pi N)^{2-d/2} e^{-\alpha} \left\{ 1 + \frac{u}{(2\pi)^2} [1 + \alpha + e^{-\alpha\zeta}/\zeta + (1 - \alpha)(\hat{\gamma} + \ln \alpha) + (\alpha - 1) Ei(-\alpha\zeta) - (1 - \alpha) \ln(2\pi N/L)] \right\} , \tag{3.9}$$

where $\alpha = R^2/2N$. Replacing u with its fixed point value $u^* = (\frac{1}{2}\pi^2)\epsilon$ and exponentiating the term of order ϵ turn Eq. (3.9) into the unnormalized macroscopically observable end-vector distribution function

$$G(N, \mathrm{R}, \theta) = (2\pi N)^{-2(1-3\epsilon/16)} L^{\epsilon/8} x^{\epsilon/8} \times \exp\left[- x^{1+\epsilon/8} + \frac{\epsilon}{8} x(1-\hat{\gamma}) + \frac{\epsilon}{8}(1+\hat{\gamma}) + \frac{\epsilon}{8}\frac{e^{-x\zeta}}{\zeta} + \frac{\epsilon}{8}(x-1)E_i(-x\zeta) - \frac{\epsilon}{8} x \ln\theta \right], \quad (3.10)$$

where x is the scaling variable defined by $x = \alpha(2\pi N\theta/L)^{-\epsilon/8}$.

B. Mean-square end-to-end distance

The mean-square end-to-end distance $\langle R^2 \rangle$ can be calculated from G given in Eq. (3.10). It is, however, far easier to calculate $\langle R^2 \rangle$ from the Fourier transform of G. Let $\tilde{G}_B(\mathrm{k}, N_0, \theta, v_0, a)$ be defined by

$$\tilde{G}_B(\mathrm{k}, N_0, \theta', v_0, a) = \int d\mathrm{R}\, G_0(N_0, \mathrm{R}, \theta; v_0, a) e^{i\mathbf{k}\cdot\mathbf{R}}. \quad (3.11)$$

Then, we have

$$\tilde{G}_B(\mathrm{k}, N_0, \theta; v_0, a) = \mathfrak{N} - \frac{1}{2d}\,\mathfrak{N}\langle R^2 \rangle k^2 + \cdots, \quad (3.12)$$

where $\mathfrak{N}$ is the normalization constant of G_B. $\tilde{G}_B$ is perturbatively calculated and Eq. (3.12) yields the bare perturbation series for $\langle R^2 \rangle$ as

$$\langle R^2 \rangle = dN_0 \left(1 + \frac{u_0}{(2\pi)^2}\left[\frac{2}{\epsilon} + \ln\frac{2\pi N_0}{L} + \ln\theta - \theta\right] + O(u_0^2)\right). \quad (3.13)$$

This quantity can be regularized when N_0 is replaced by N with the same choice of Z_2:

$$\langle R^2 \rangle = dN\left(1 + \frac{u}{(2\pi)^2}\left[\ln\frac{2\pi N}{L} + \ln\theta - \theta\right]\right). \quad (3.14)$$

Exponentiation and setting $u = u^*$ as in the case of G gives

$$\langle R^2 \rangle = dN\left(\frac{2\pi M}{L}\right)^{\epsilon/8} e^{-\epsilon M/8N}, \quad (3.15)$$

where $\theta = M/N$ has been used.

IV. RESULTS AND DISCUSSION

Normalizing Eq. (3.10) as the distribution function for the vector R yields

$$P_N(\mathrm{R}, \theta) = (2\pi N)^{-2+\epsilon/4} L^{\epsilon/4} \theta^{-\epsilon/4} x^{\epsilon/8} \times \exp\left\{\frac{\epsilon}{8}\left(\hat{\gamma} + \ln\frac{\zeta}{1+\zeta} - \frac{1}{\zeta}\right) - x^{1+\epsilon/8} + \frac{\epsilon}{8}\left[x(1-\hat{\gamma}) + e^{-x\zeta}/\zeta - x\ln\frac{\zeta}{1+\zeta} + (x-1)Ei(-x\zeta)\right]\right\}. \quad (4.1)$$

This form is convenient when θ is nearly unity, i.e., when the chain is almost self-avoiding. In the $\theta \to 0$, $(\zeta \to 0)$ limit, Eq. (4.1) reduces to the Gaussian distribution function with the average given by $\langle R^2 \rangle = dN(2\pi M/L)^{\epsilon/8}$ after some rearrangement of order ϵ terms. To see these limiting cases more explicitly, the following form is helpful:

$$P_N(\mathrm{R}, \theta) = (2\pi N)^{-2+\epsilon/4} L^{\epsilon/4} \theta^{-\epsilon/4} x^{\epsilon(1-\exp(-x\zeta))/8} \times \exp\left[- x^{1+\epsilon(1-\exp(-x\zeta))/8} + \frac{\epsilon}{8}\left\{\frac{e^{-x\zeta}-1}{\zeta} + x\right\} + \frac{\epsilon}{8}(x-1)\left\{Ei(-x\zeta) - \hat{\gamma} - \ln\frac{\zeta}{1+\zeta} - e^{-x\zeta}\ln x\right\}\right]. \quad (4.2)$$

In the $\theta \to 1$ (SAW) limit, Eq. (4.2) reduces to the distribution function for the full self-avoiding polymer chain. In the opposite $\theta \to 0$ limit, all the factors in curly brackets disappear, so that if $M = N\theta$ is reintroduced, Eq. (4.2) turns out to be

$$P_N(\mathrm{R}, \theta) = (2\pi N)^{-2+\epsilon/2} (2\pi M/L)^{-\epsilon/4} \times \exp\left(-\frac{R^2}{2N}(2\pi M/L)^{-\epsilon/8}\right), \quad (4.3)$$

as is stated before. In the $\theta \to 0$ limit, one might expect the unperturbed distribution function to be recoved. The reason for the difference between Eq. (4.3) and the unperturbed distribution function is as follows. The renormalization group technique employed requires that $M = N\theta$ must be far larger than a. Therefore, cases with very small M cannot be studied by this method. The limit $\theta \to 0$ implies $N \gg M \gg a$. Hence, what is recovered in the limit from Eq. (4.2) cannot be the unperturbed form. In this limit, N is asymptotically much larger than M, and the chain becomes Markovian, so the distribution function becomes Gaussian.

The apparently strange behavior of the mean-square end-to-end distance can also be understood in the same fashion. Equation (3.15) can be rewritten as

$$\langle R^2 \rangle = \langle R^2 \rangle_{\mathrm{SAW}} \theta^{\epsilon/8} \exp\left[\frac{\epsilon}{8}(1-\theta)\right], \quad (4.4)$$

where $\langle R^2 \rangle_{\mathrm{SAW}}$ is $\langle R^2 \rangle$ for the self-avoiding chain already given in paper III. Equation (4.4) apparently shows that in the $\theta \to 0$ limit $\langle R^2 \rangle$ becomes zero. However, as is already explained, this limit requires very large N. Since the chain in this limit is Markovian, so $\langle R^2 \rangle$ is

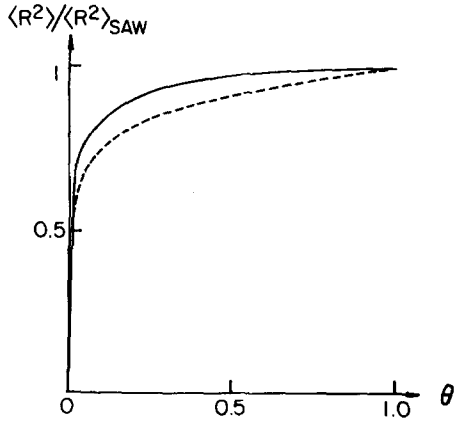

FIG. 1. The ratio $\langle R^2 \rangle / \langle R^2 \rangle_{\mathrm{SAW}}$ as a function of $\theta = M/N$, the relative order of FSAW. —— shows the result to order ϵ given by Eq. (4.4). ---- is $\langle R^2 \rangle = \langle R^2 \rangle_{\mathrm{SAW}} \theta^{\epsilon/8}$ which is the result of the simple scaling argument. The scaling argument overestimates the difference of FSAW and SAW.

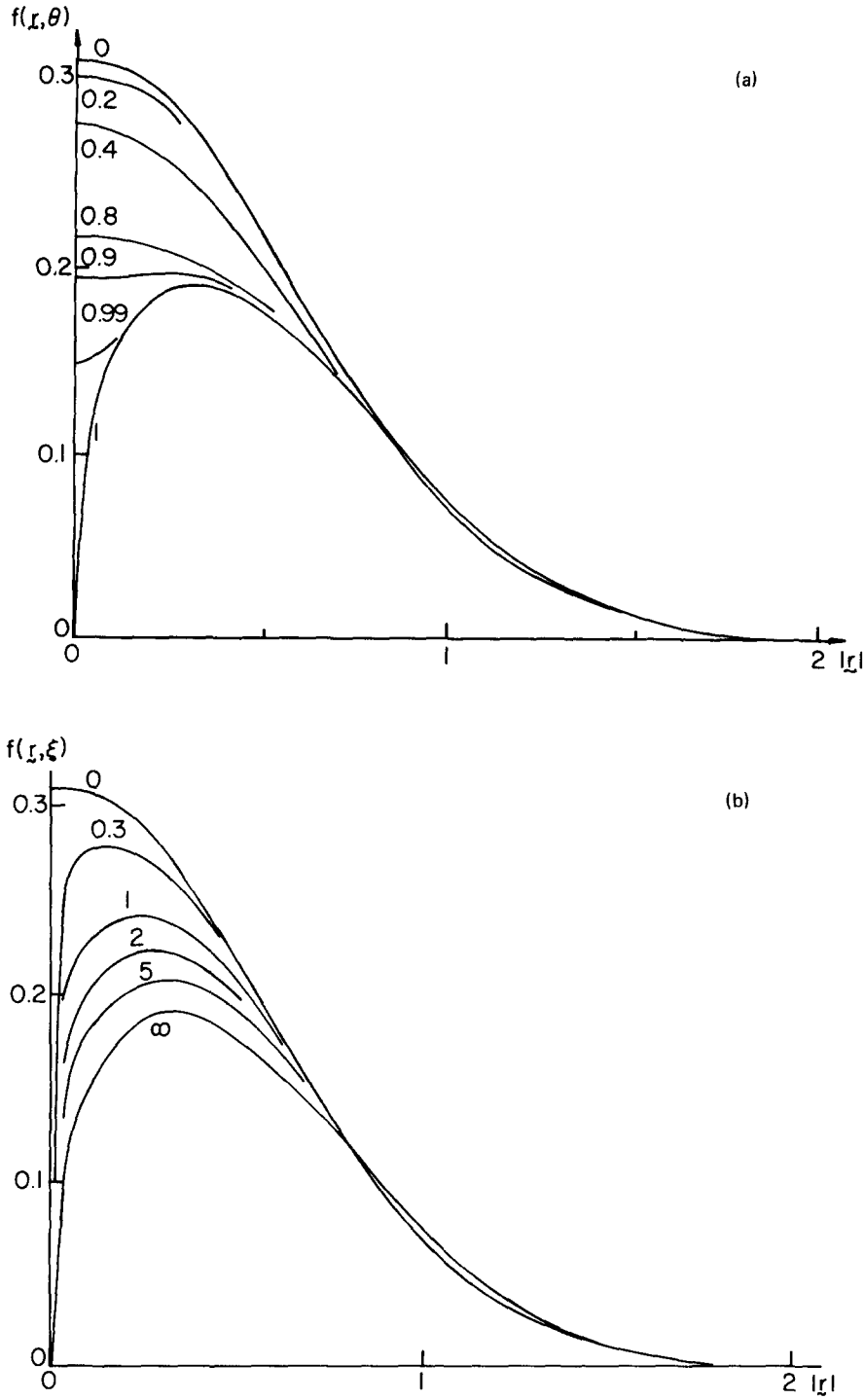

FIG. 2. (a) The distribution function $f(\mathbf{r}, \theta)$ given by Eq. (4.6) for several θ values. The numbers in the figure denote θ. Note that even if $\theta = 0.99$, the behavior of $f(\mathbf{r}, \theta)$ for smaller $\mathbf{r}$ is markedly different from the $\theta = 1$ SAW case. (b) The distribution function of $\mathbf{r}$ for route M, where the numbers in the figure denote ξ, a renormalization group theoretic counterpart of the conventional z parameter. See Ref. 5 for details. $\xi = 0$ is the simple random walk and $\xi = \infty$ is the full SAW. Except in the case of vanishing ξ, all $f(\mathbf{r})$ are zero at the origin reflecting the global repulsive interaction between two monomers on the chain.

proportional to N. On the other hand, $\langle R^2\rangle_{\text{SAW}} \propto N^{2\nu}$ with $2\nu > 1$. Hence the ratio $\langle R^2\rangle/\langle R^2\rangle_{\text{SAW}}$ must vanish in the $\theta \to 0$ limit. A simple scaling argument for $\langle R^2\rangle$ is as follows. $\langle R^2\rangle/\langle R^2\rangle_{\text{SAW}}$ must be a function of θ alone; $\langle R^2\rangle = \langle R^2\rangle_{\text{SAW}} f(\theta)$. If $M \ll N$, then $\langle R^2\rangle \propto N$, so that $N^{2\nu}\theta^x \propto N$ in this limit. Thus, we have

$$\langle R^2\rangle \propto \langle R^2\rangle_{\text{SAW}} \theta^{2\nu-1} . \tag{4.5}$$

Therefore, the additional factor $\exp[\epsilon(1-\theta)/8]$ in Eq. (4.4) cannot be given by simple scaling argument. The ratio $\langle R^2\rangle/\langle R^2\rangle_{\text{SAW}}$ is shown in Fig. 1 for the FSAW in three space.

Equation (4.4) shows that when θ is fixed, $\langle R^2\rangle \propto N^{2\nu}$ no matter how small $\theta(>0)$ is. According to the conventional approach to the excluded volume problem, the contribution from the intrachain interaction between monomers far apart from each other in contour distance is the most important factor to change the exponent from 1 to $2\nu > 1$. However, the observation stated above clearly disagrees with this conventional idea.

When the spatial coordinates are rescaled by $\langle R^2\rangle^{1/2}$, $P_N(\mathbf{R}, \theta)$ will become universal function $f(\mathbf{r}, \theta)$ of $\mathbf{r} = \mathbf{R}/\sqrt{\langle R^2\rangle}$ and θ,

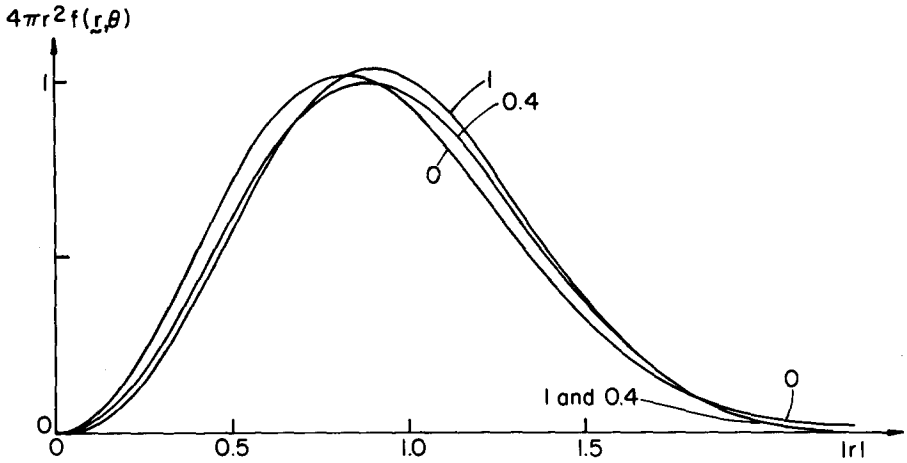

FIG. 3. The distribution of $r = |\mathbf{r}|$ in three space. Because of the factor $4\pi r^2$, the θ dependence of $f(\mathbf{r}, \theta)$ is greatly reduced. The numbers in the figure denote θ. For $0 < \theta < 1$, $4\pi r^2 f(\mathbf{r}, \theta)$ is somewhat broad, and as is expected, for smaller r, it behaves like the simple random walk ($\theta = 0$) and for larger r like the full SAW ($\theta = 1$).

$$f(\mathbf{r},\theta) = (d/2\pi)^{d/2}(2r^2)^{\epsilon[1-\exp(-2r^2\zeta)]/8} \times \exp\left[-\frac{\epsilon}{4}\theta - (2r^2)^{1+\epsilon[1-\exp(-2r^2\zeta)]/8}\left(1-\frac{\epsilon}{4}-\frac{\epsilon}{8}\theta\right) + \frac{\epsilon}{8}\frac{e^{-2r^2\zeta}-1}{\zeta} + 2r^2\right\} + \frac{\epsilon}{8}(2r^2-1)\left\{Ei(-2r^2\zeta) - \hat{\gamma} - \ln[\zeta/(\zeta+1)] - e^{-2r^2\zeta}\ln(2r^2)\right\}\Bigg]. \quad (4.6)$$

In the $\theta \to 1$ limit, Eq. (4.6) reduces to the distribution function for SAW given by Eq. (5.5) of paper III. In the $\theta \to 0$ limit, Eq. (4.6) gives the simple Gaussian distribution function. The functions $f(\mathbf{r}, \theta)$ in three space for several values of θ are given in Fig. 2(a). For comparison, the crossover behavior of the distribution functions $f(\mathbf{r})$ of $\mathbf{r} = \mathbf{R}/\sqrt{\langle R^2\rangle}$ via route M is shown in Fig. 2(b). Along route M $f(\mathbf{r})$ always vanishes at the origin, while along route R, $f(\mathbf{r}, \theta)$ is always positive at the origin whenever θ is less than 1,

$$f(0,\theta) = (d/2\pi)^{d/2}(1-\theta)^{\epsilon/8}\, e^{-\epsilon\theta/4}\,. \quad (4.7)$$

Also $4\pi r^2 f(\mathbf{r}, \theta)$ for $\theta = 0$, 0.4, and 1 are given in Fig. 3.

As we have already mentioned in the introduction, FSAW can be considered as a mathematical model of the "blob" picture introduced by de Gennes in order to explain the crossover behavior from dilute to semidilute solution regime with good solvents. As is stated in the Introduction, the distribution function of the end-to-end vector R of a test chain is not faithfully described by that of a FSAW chain. For example, the former always vanishes at the origin irrespective of the concentration of the semidilute solution. Still, as has been suggested by the scaling argument, there are some asymptotic cases where $\langle R^2\rangle$ can be understood in terms of FSAW. The $\langle R^2\rangle$ for a test chain of length N immersed in the semidilute solution of chains of the (number) average length $\langle N\rangle$ and $M_w/M_n = \mu^{-1}$ is given to order ϵ in the large chain overlap limit by[18,9]

$$\langle R^2\rangle \sim N^{1+\epsilon(1-X/(\mu+X))/8}\langle N\rangle^{\epsilon X/8(\mu+X)}(\mu+X)^{-\epsilon X/8(\mu+X)} \sim \langle R^2\rangle_{\mathrm{SAW}}(\langle N\rangle/NX)^{\epsilon/8}\,, \quad (4.8)$$

where

$$X \propto c\langle N\rangle^{d\nu}, \quad \nu = (1+\epsilon/8+\cdots)/2\,,$$

and c is the concentration of chains of average length $\langle N\rangle$. Therefore, in the large chain overlap limit ($X \gg 1$) $\langle R^2\rangle$ behaves exactly as Eq. (4.5) with $M = \langle N\rangle/X$ which is in agreement with the scaling argument to order ϵ.

Detailed comparison of FSAW with the test chain in the semidilute solution will be given in the forthcoming paper.

V. SUMMARY

The chain conformation space renormalization group method of Oono, Ohta and Freed[11] has been used to calculate the end-vector, distribution function for a finite order self-avoiding random walk. Since, in the present case, the interaction is contour length dependent, the polymer–magnet analogy is of little use. On the other hand, the calculations are very simple and transparent in the chain-conformation space RG approach. Thus, the calculation is a good example of the power and elegance of this RG method.

The comparison of two conceptually very different routes R (range) and M (magnitude) connecting simple random walk behavior and self-avoiding walk behavior of a chain is given. For FSAW, the end-vector distribution function is positive at the origin, but for chains along route M it always vanishes at the origin. The blob argument is mathematically modeled as FSAW, but, strictly speaking, the behavior of the distribution function near the origin for a test chain immersed in the semidilute solution is different from that for FSAW. The significance of the difference will be considered in a forthcoming paper.

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