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Flexible Polymer with Excluded Volume at an Interacting Penetrable Surface of Variable Dimension: A Multiple-ϵ Perturbation Theory

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ABSTRACT: Application of the renormalization group method to the perturbative treatment of surface interacting polymers with excluded volume currently requires the surface dimension to be fixed. A multiple-ϵ perturbation expansion method is proposed to circumvent this technical restriction. There are numerous potential applications of multiple-ϵ perturbation theory (e.g., combined treatment of binary and ternary excluded volume interactions) which can be pursued once the internal consistency of the method is demonstrated in higher order calculations. The surface interaction model provides a good starting point for studying the multiple-ϵ method because of the relative simplicity of the perturbative calculations that provide the input into the multiple-ϵ renormalization group calculations. Another convenient aspect of the model is that the consistency of the multiple-ϵ method can be checked against accurate results for the limits of each interaction (surface and excluded volume) alone and the combined interactions for the special case of a two-dimensional surface.

1. Introduction

The theoretical description of isolated polymers in the presence of an interacting boundary has been considered by using both lattice random walk and continuum Gaussian chain models. Rubin[1] and Hammersley[2] studied random walks interacting with surfaces of varying dimension $d_\parallel$ (point, $d_\parallel = 0$; line, $d_\parallel = 1$; etc.) and calculated many of the important configurational properties of ideal polymers with no polymer–polymer interactions. There are complementary studies for the continuum model formulation of surface ($d_\parallel = 2$) interacting Gaussian chains at an impenetrable surface,[3] and numerous calculations address the problem of surface interacting chains with excluded volume[4-9] (see below).

Recent calculations by Kosmas[6] and Douglas et al.[7] consider the problem of a surface interacting chain from the general perspective where the interacting surface is taken to have a continuously variable dimension. Initial calculations by Kosmas[6] introduced the model and utilized a version of the renormalization group (RG) theory to calculate certain exponents characterizing the number of polymer configurations subject to the surface constraint. More recent calculations by Douglas et al.[7] give *exact* calculations for many configurational properties over the full range (attractive and repulsive) of surface interactions, which they then compare with the corresponding scaling functions obtained using the approximate Gell-Mann–Low RG theory. Those calculations enable the unambiguous estimation of ϵ-expansion errors in the scaling functions order by order in ϵ perturbation theory and are also useful for understanding the characteristic failure of the RG theory to describe polymers with attractive polymer–polymer or polymer–surface interactions.[7]

Both Kosmas[6] and Douglas et al.[7] have applied the RG schemes to treat the combined influence of polymer excluded volume and surface interactions for the special case where the surface dimension is fixed at two dimensions so that the ϵ-expansion method can be applied to both interactions. Kosmas' calculation[6] emphasizes the combined effect of surface and excluded volume interactions on the exponents that characterize the number of chain configurations, while the work of Douglas et al.[7] describes the effect of excluded volume on the scaling functions of configurational properties such as the end vector distance $\langle \mathbf{R}^2 \rangle$ in relation to the properties calculated without excluded volume. Of course, the combined treatment of polymer excluded volume and surface interactions necessarily becomes approximate once excluded volume is incorporated into the theory and is then primarily restricted to repulsive polymer–polymer and polymer–surface interactions.

Despite the extensive work that has been done on surface interacting chains, there are numerous important problems that remain. For example, the effect of surface proximity[8] of a particular chain to the surface, polymer confinement to a finite region with interacting boundaries,[8]

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and the effect of surface curvature on polymer dimensions[8] are effects that have only begun to be considered. Moreover, there are many issues involving the "connectedness" of the interacting surface, and there is the obvious problem of a polymer interacting with "fractal sets"—corresponding physically to randomly distributed solution impurities, diffuse interfaces between media, etc.

The surface interaction model, where the surface is taken to have a variable dimension, provides many *qualitative* insights[7] into these remaining problems. Unfortunately, however, the available RG methods require the surface dimension to be *fixed* when excluded volume is incorporated into the theory.[5-9] Calculations for impenetrable surfaces[5,8,9] generally take the surface dimension $d_\parallel$ equal to $d - 1$, where d is the dimension of space while, alternatively, the calculations of Kosmas[6] and Douglas et al.[7] with excluded volume fix the surface dimension as $d_\parallel = 2$.

The main objective of the present work is to obtain a scheme for describing flexible surface interacting polymers with repulsive polymer–polymer and polymer–surface interactions where the surface dimension is *not fixed*. The mathematical problem involved in this generalization is a fundamental one that arises frequently in calculations where there are multiple interactions. Characteristically, the various types of polymer interactions depend strongly on the segment density, which in turn depends on the dimension of space. Typically, there are "upper critical dimensions" for the different interactions above which it is no longer necessary to consider the effect of the given interaction in the long-chain limit. For example, the excluded volume problem is well-known[10,11] to have the critical dimension of 4, which, of course, occurs because the chain density is so low above $d = 4$ that the repulsive excluded volume interactions can be reasonably treated as negligible. The theoretical treatment using the RG is straightforward when there is one interaction, as in the case of excluded volume, or even multiple interactions having the same critical dimension, as in the case of polymer excluded volume effects on hydrodynamic properties[12,13] or the multiple excluded volume interactions that arise in block copolymers and mixtures.[14-16] Several situations occur, however, in which the multiple interactions *do not* have the same critical dimension. This notoriously difficult problem arises in the area of polymer physics, for example, in the instance of a polymer with both binary and ternary excluded volume interactions since ternary interactions have a critical dimension of 3.[17-19] Other examples are discussed in the Appendices and below.

Despite the central importance of the description of the combined influence of binary and ternary interactions, all calculations to date are restricted to infinitesimal binary interaction (very near the Flory Θ point) and *only* ternary interactions are allowed to vary over a large range. Lawrie makes some valiant attempts[20,21] to treat the general $\mathcal{O}(n)$ field theoretic analogue of polymers with binary and ternary interactions in which ϵ-expansions for both interactions are developed about 4 or, alternatively, 3 dimensions.[20,21] Although very interesting, these calculations do not unambiguously resolve the matter. Oono[22] has introduced a theoretical framework, the "homotopy expansion", which provides another promising approach to this general problem.

The situation of multiple interactions having differing critical dimensions occurs frequently in polymer physics and many other areas of physics where there are multiple competing interactions. It is shown in previous work[6,7] that for Gaussian chains interacting with a surface the critical dimension is $d_c = 2 + d_\parallel$, which is coincident with the critical dimension of the excluded volume problem *only* when $d_\parallel$ is fixed as 2. Fixing $d_\parallel = 2$ enables the application of standard RG methods to the description of the combined effect of both interactions on polymer properties.[6,7] Formally, there are *two* critical dimensions in the problem when $d \neq 2$, and this problem is approached here by pursuing a *double expansion* in two ϵ-parameters. This method has the virtue of reducing (by definition) to the ϵ-expansion of each interaction alone, which is not the case if a *single* critical dimension is artificially used for both interactions.[20,21] Although no trouble is found in treating multiple interactions with multiple ϵ's to leading order, it is warned that there is *no proof* of the consistency of the method to higher order in perturbation theory. At present the method is presented only as a *possible computational scheme* for this very important class of problems. Kosmas and Douglas[4] give a brief description of the multiple-ϵ scheme for surface interacting polymers with excluded volume using the alternate reexponentiation RG method introduced by Kosmas.[6]

2. Model

The polymer is modeled by a continuous Gaussian chain specified by a position vector $\mathbf{R}(x)$ at a contour distance x along a chain of unit length N. The chain is composed of n Kuhnian links of length l, $N = nl$, and has a mean-square end-to-end distance of $\langle \mathbf{R}^2 \rangle_{0,f} = nl^2$ in the absence of interactions (a "free" chain). In the units of $K_B T$, the unperturbed Hamiltonian is

$$\mathcal{H}_0 = \tfrac{1}{2} \int_0^1 dx\, |d\mathbf{r}(x)/dx|^2 \qquad (2.1)$$

$$\mathbf{r}(x) = (d/\langle \mathbf{R}^2 \rangle_{0,f})^{1/2} \mathbf{R}(x)$$

Next, we add a pseudopotential (δ function) surface interaction in dimensionless units:[6,7]

$$\mathcal{H}_s(\text{polymer–surface}) = z_s^\circ \int_0^1 dx\, \delta[\mathbf{r}_\perp(x)](2\pi)^{d_\perp/2} \qquad (2.2)$$

$$z_s^\circ = (d/2\pi l^2)^{d_\perp/2} \beta_s^\circ n^{\phi_s^\circ}; \quad \phi_s^\circ = \epsilon_\perp/2 \qquad (2.3)$$

$$\epsilon_\perp = 2 - d_\perp = (2 + d_\parallel) - d; \quad d_\perp + d_\parallel = d \qquad (2.4)$$

where the surface is an Euclidean hypersurface of dimension $d_\parallel$ embedded in a space of dimension d, β_s° is a surface interaction coupling constant, and ϕ_s° is the crossover exponent for a Gaussian surface interacting chain. The position vectors $\mathbf{R}_\perp$ and $\mathbf{R}_\parallel$ and their dimensionless counterparts

$$\mathbf{r}_\parallel(x) = (d/\langle \mathbf{R}^2 \rangle_{0,f})^{1/2}\, \mathbf{R}_\parallel(x);$$
$$\mathbf{r}_\perp(x) = (d/\langle \mathbf{R}^2 \rangle_{0,f})^{1/2}\, \mathbf{R}_\perp(x) \qquad (2.5)$$

are the projections of $\mathbf{R}$ onto the $d_\parallel$ dimension surface and the "orthogonal" space of dimension $d_\perp$. For concreteness the surface dimension $d_\parallel = 0$, $d_\parallel = 1$, etc., corresponds to a point, line, etc., and having variable $d_\parallel$ provides a convenient way for describing the effect of surface dimension in a unified way. A crude description of an "irregular" (fractal) surface may be obtained by identifying $d_\parallel$ with the fractal dimension of the surface.[7]

There are also polymer–polymer excluded volume interactions that should be considered. Here attention is confined to binary excluded volume interactions[23] (the two-parameter model):

$$\mathcal{H}_2(\text{polymer–polymer}) =$$
$$(z_2^\circ/2!) \int_0^1 dx \int_0^1 dx'\, \delta[\mathbf{r}(x) - \mathbf{r}(x')](2\pi)^{d/2} \qquad (2.6)$$

$$z_2^\circ = (d/2\pi l^2)^{d/2}\beta_2^\circ n^{\phi_2};\quad \phi_2 = \epsilon/2;\quad \epsilon = 4 - d \tag{2.7}$$

where β_2° is the excluded volume coupling constant.

3. Perturbative Calculations and Review of Single-ϵ Method

Configurational properties calculated for the surface interacting polymer with excluded volume are described in previous work. Basically, the idea is to expand the full Hamiltonian in a formal Taylor series in z_2° and z_s° to obtain

$$\exp(-\mathcal{H}/K_BT) = \exp(-\mathcal{H}_0)[1 - \mathcal{H}_s - \mathcal{H}_2 + \mathcal{O}(\mathcal{H}_s^2,\mathcal{H}_s\mathcal{H}_2,\mathcal{H}_2^2)] \tag{3.1}$$

Configurational averages for the series (3.1) can be solved exactly for $z_2^\circ = 0$ through infinite order, and results are given by Douglas et al.[7] The calculations of the double expansion in $\mathcal{H}_s$ and $\mathcal{H}_2$, of course, are more difficult. For example, the mean-square normal distance $\langle \mathbf{R}_\perp^2 \rangle$ of a terminally attached chain at an interacting penetrable surface for a chain with excluded volume interactions is given by[7]

$$\langle \mathbf{R}_\perp^2 \rangle = (d_\perp/d)\langle \mathbf{R}^2 \rangle_{0,f}[1 + z_s^\circ + (2/\epsilon - 1)z_2^\circ + (2/\epsilon_\perp)(z_s^\circ)^2 + (-6/\epsilon^2 + 11/2\epsilon)z_2^\circ + ...] \tag{3.2}$$

where we neglect the second-order cross term $z_2^\circ z_s^\circ$ since it is nonsingular in either ϵ or $\epsilon_\perp$. This contribution does not contribute to our leading order calculation (see ref 6 and 7).

Note that (3.2) contains formal poles in *both* $\epsilon = 4 - d$ and $\epsilon_\perp = 2 + d_\parallel - d$. In a previous calculation, the special case of $d_\parallel = 2$ ($\epsilon_\perp = \epsilon$) is considered where (3.2) reduces to

$$\langle \mathbf{R}_\perp^2 \rangle = (d_\perp/d)\langle \mathbf{R}^2 \rangle_{0,f}[1 + z_s^\circ + (2/\epsilon - 1)z_2^\circ + (2/\epsilon)(z_s^\circ)^2 + (-6/\epsilon^2 + 11/2\epsilon)(z_2^\circ)^2 + ...] \tag{3.3}$$

The RG method then proceeds in a standard fashion,[24] which is schematically reviewed because it becomes a point of reference in the generalized method introduced below. First, introduce dimensionless coupling constants u_s° and u_2° for the polymer–surface and excluded volume interactions as

$$z_2^\circ = u_2^\circ(2\pi N/L)^{\epsilon/2} \tag{3.4a}$$

$$z_s^\circ(d_\parallel = 2) = u_s^\circ(2\pi N/L)^{\epsilon/2} \tag{3.4b}$$

where L is an intermediate model variable having the dimensions of length. Renormalization constants are then introduced for the dimensionless coupling constants u_2°, u_s°, and the chain length, N_0:

$$u_s^\circ = u_s Z_{u_s};\quad Z_{u_s} = 1 + 2u_2/\epsilon + 2u_s/\epsilon + \mathcal{O}(u_s^2,u_2u_s,u_2^2) \tag{3.5a}$$

$$u_2^\circ = u_2 Z_{u_2};\quad Z_{u_2} = 1 + 8u_2/\epsilon + \mathcal{O}(u_2^2) \tag{3.5b}$$

$$N_0 = NZ_N^{-1};\quad Z_N = 1 + 2u_2/\epsilon + \mathcal{O}(u_2^2) \tag{3.5c}$$

All of the formal singularities are removed when the definitions (3.4) and (3.5) are introduced into the expansion (3.3). This leads to the remarkably simple result to first order in ϵ:

$$\langle \mathbf{R}_\perp^2 \rangle = (d_\perp/d)\langle \mathbf{R}^2 \rangle_f(1 + u_s) + \mathcal{O}(\epsilon^2) \tag{3.6a}$$

where u_s is the "renormalized coupling constant" defined in (3.5a) (now a function of the excluded volume) and $\langle \mathbf{R}^2 \rangle_f$ is the end-vector distance for a "free" chain *with* excluded volume. Douglas et al.[7] argue that (3.6a) should be rewritten (consistent to order ϵ) as

$$\langle \mathbf{R}_\perp^2 \rangle = (d_\perp/d)\langle \mathbf{R}^2 \rangle_f/(1 - u_s) + \mathcal{O}(\epsilon^2) \tag{3.6b}$$

which is *exact*[7] for $z_s^\circ \to \infty$ and $z_2^\circ = 0$. The Gell-Mann–Low β functions are obtained by taking derivatives of the renormalization constants and in a standard fashion. Douglas et al. obtain to leading order[7,24]

$$\beta_2(u_2) = (\epsilon/2)u_2(1 - 8u_2/\epsilon) \tag{3.7a}$$

$$\beta_s(u_2,u_s) = (\epsilon/2)u_s(1 - 2u_s/\epsilon - 2u_2/\epsilon) \tag{3.7b}$$

These fixed points are the same as those determined by Kosmas[6] except that Kosmas' definition of u_2^* differs from ours by a factor of 2. For reference below,[7] the fixed points [nontrivial zeros of (3.7a) and (3.7b)] are defined as

$$(u_2^*,u_s^*) = (0,0);\quad (0,\epsilon/2);\quad (\epsilon/8,0);\quad (\epsilon/8,3\epsilon/8) \tag{3.8}$$

The first fixed point corresponds to Gaussian chains and no surface interactions, the second to Gaussian chains with strong surface repulsion, the third to chains with strong excluded volume and no surface interaction, and the last to chains with large excluded volume and surface interactions. The interactions are assumed to be *repulsive* only. Inserting u_s^* calculated in this way into (3.6b) gives[7] the limiting values of the dimensionless ratio $\gamma_{\mathbf{R}_\perp}^2 \equiv \langle \mathbf{R}_\perp^2 \rangle/(d_\perp/d)\langle \mathbf{R}^2 \rangle_f$ as ($d = 3$, $d_\parallel = 2$):

$$\gamma_{\mathbf{R}_\perp}^2(u_s^*=0) = 1 \quad \text{(exact)} \tag{3.9a}$$

$$\gamma_{\mathbf{R}_\perp}^2(u_s^*=\epsilon/2;\ u_s^*=0) = 2 \quad \text{(exact)} \tag{3.9b}$$

$$\gamma_{\mathbf{R}_\perp}^2(u_s^*=3\epsilon/8;\ u_2^*=\epsilon/8) = 8/5 \quad \text{(first order in } \epsilon) \tag{3.9c}$$

4. Perturbative Renormalization

There is no difficulty in treating multiple ϵ-parameters at the level of perturbative theory if the calculations are performed without ϵ-expansion. The problem comes at the level of introducing renormalization constants, where a *fundamentally new technique is needed.*

Assuming for a moment that a more general renormalization method exists, we can examine the limiting situations that such a scheme would have to recover as special cases. We can treat the surface interaction problem with variable $d_\perp$ and no excluded volume by introducing the renormalization constant defined by

$$Z_{u_s}(u_2=0) = 1 + 2u_s/\epsilon_\perp + (2u_s/\epsilon_\perp)^2 + ... \tag{4.1}$$

Both (3.5a) and (4.1) are consistent *provided* we have the double expansion in $u_s/\epsilon_\perp$ and u_2/ϵ. This observation leads to

$$Z_{u_s}(u_2,u_s) = 1 + 2u_s/\epsilon_\perp + 2u_2/\epsilon + ... \tag{4.2}$$

which is taken for the generalization required by consistency. Insertion of $Z_{u_s}(u_s/\epsilon_\perp,u_2/\epsilon)$, defined in this way, along with Z_{u_2} and Z_N leads to (3.5a–c), except that (3.5a) is now more generally given by (4.2).

It should be evident that the procedure becomes rather tricky as we try to go to higher order, since it is not obvious whether (nonsingular) dimensional factors should be written as a function of ϵ or $\epsilon_\perp$. At this point, it is simply assumed that this technical matter can be sorted out, and as a consequence the proposed method can be presented only as a tentative, promising one. The existence of renormalizability and the consistency with conventional theory for the limit $\epsilon = \epsilon_\perp$ put constraints on the interpretation of the higher order theory in terms of ϵ and $\epsilon_\perp$.

The definition of the surface interaction Gell-Mann–Low function to leading order (see Appendix A) implies

$$\beta_s(u_2,u_s) = (\epsilon_\perp/2)u_s[1 - 2u_s/\epsilon_\perp - 2u_2/\epsilon_\perp] \tag{4.3}$$

which has the nontrivial fixed point

$$u_s^*(u_2) = u_{s,0}^* - u_2 + \mathcal{O}(\epsilon_2,\epsilon_\perp\epsilon); \quad u_{s,0}^* = \epsilon_\perp/2 \tag{4.4}$$

corresponding to the vanishing of β_s. Kosmas and Douglas[4] have obtained the same fixed point condition (4.4) by generalizing the alternate "exponentiation technique" method of renormalization utilized by Kosmas in his earlier calculations for surface ($d_\parallel = 2$) interacting chains with excluded volume. It is noted that (4.4) was derived in Kosmas and Douglas[4] from a second-order calculation of the partition function within the Kosmas RG formalism, while here it is derived from a second-order calculation of $\langle \mathbf{R}^2 \rangle$. To leading order the excluded volume interaction remains "decoupled" from the surface interaction and β_2 and Z_{u_2} are independent of u_s. The β function β_2 is the *same* as in (3.7a). The authors believe this will be true through all orders in perturbation theory.

Now, although the introduction of (4.2) seems to provide a scheme for cancelling the leading order poles in ϵ and $\epsilon_\perp$, the final results seem (at first!) rather peculiar. Note the u_2 term in (4.3) has a pole in $\epsilon_\perp$ rather than ϵ as expected. It also seems strange that if $\epsilon_\perp = 0$ (corresponding to a polymer interacting with a line in three dimensions) the fixed point u_s^* is then formally *negative*. It is very doubtful, however, that a negative fixed point can have any physical significance. It is this observation that hints at how we should proceed further.

5. Variable Critical Dimension of Surface Interacting Chain with Excluded Volume

Some insight into the peculiar form of (4.3) can be gained by considering another situation where a negative fixed point is obtained. For a Gaussian chain ($u_2 = 0$) interacting with its endpoint ($d_\parallel = 0$) in three dimensions, we *formally* have

$$u_{s,0}^* = \epsilon_\perp/2 = -1/2 \tag{5.1a}$$

The surface interaction in this instance scales [see (2.3)] as

$$z_s^\circ \sim n^{-1/2} \tag{5.1b}$$

and in the long-chain limit the surface interaction becomes negligible corresponding physically to $u_s^* = 0$. The occurrence of a negative fixed point in this exactly solvable case means that we are above the critical dimension where the RG theory is quite meaningless!

Since u_s^* for *perturbed chains* does not vanish at the same dimension as it does for Gaussian chains, we are led to expect that the *critical dimension is itself a function of the excluded volume interaction.* The presence of a negative fixed point u_s^* is consistent with excluded volume *lowering* the critical dimension.

An estimate for how the critical dimension shifts may be obtained from a scaling argument. Scaling the surface interaction by the chain dimensions of a free chain *with* excluded volume $\langle \mathbf{R}^2 \rangle_f$ gives

$$\mathcal{H}_s = \hat{z}_s \int_0^1 dx\ \delta[\hat{\mathbf{r}}_\perp(x)](2\pi)^{d_\perp/2} \tag{5.2}$$

$$\hat{\mathbf{r}}_\perp(x) = (d/\langle \mathbf{R}^2 \rangle_f)^{1/2} \mathbf{R}_\perp(x)$$

with the dimensionless interaction defined as

$$\hat{z}_s = (d/2\pi)^{d_\perp/2} \beta_s^\circ n \langle \mathbf{R}^2 \rangle_f^{-d_\perp/2} \tag{5.3}$$

where $\hat{z}_s(z_2^\circ = 0) = z_2^\circ$ as defined in (2.3). For a large excluded volume interaction, the mean dimensions scale as a power law $\langle \mathbf{R}^2 \rangle_f \sim N^{2\nu}$, so that $\hat{z}_s$ scales as[7]

$$\hat{z}_s \sim n^{\phi_s}; \quad \phi_s = 1 - d_\perp \nu; \quad z_2^\circ \gtrsim 1 \tag{5.4}$$

A special case of this scaling argument corresponding to $d_\perp = 1$ is known as the Bray–Moore conjecture.[26]

The scaling argument to obtain (5.4) assumes the *penetrable* surface model. Comparison with simulations on *impenetrable* surfaces and with RG calculations for an impenetrable surface indicate that (5.4) is *not correct* when there is excluded volume.[27] This should not be too surprising, since surface impenetrability is equivalent[28] to having an additional surface interaction that biases the chain to lie on one side of the $d_\parallel = d - 1$ hypersurface. First-order RG calculations for the penetrable surface[7] ($d_\parallel = 2$) are consistent with (5.4), and simulation data for the *penetrable* surface are also consistent.[29] The crossover exponent given by (5.4) is believed to be *exact* for penetrable surfaces,[28] and it is emphasized that *only penetrable surfaces are being considered here.*

We are now in a position to investigate the origin of the (formal) negative fixed point for $d_\perp = 2$ and swollen chains in (4.4). It is clear that ϕ_s in (5.4) is negative for all $\nu > {}^1/_2$, and the negative fixed point simply arises because of a reduction of the surface interaction critical dimension. Specifically, the critical dimension may be *defined* by the vanishing of ϕ_s, and this condition in (5.4) implies that the surface interaction critical dimension $d_{\perp,c}$ is given by

$$d_{\perp,c} = 1/\nu \qquad \text{(swollen chains)} \tag{5.5}$$

Taking ν to have the Flory value for simplicity implies

$$d_{\perp,c} \approx (d + 2)/3 \qquad \text{(swollen chains)} \tag{5.6}$$

The physical origin of the lowering of the surface interaction critical dimension becomes obvious if we consider the special case of $d = d_\perp$, corresponding to a chain interacting with a point.[30] For random walks ($\nu = {}^1/_2$) the critical dimension is 2, reflecting the well-known property that random walks return to the origin (or an arbitrary point taken on the chain) with a probability less than unity for $d > 2$. The addition of excluded volume means that even in $d = 2$, the probability of return to a point is diminished.

6. Introduction of a Variable $\epsilon_\perp$-Parameter

The preceding discussion on the variability of the surface interaction with the fractal dimension[31] ($d_f = 1/\nu$) of the coil provides motivation for the definition of an excluded volume dependent $\epsilon_\perp$-parameter as

$$\epsilon_\perp' \equiv 1/\nu - d_\perp = (1/\nu + d_\parallel) - d \tag{6.1}$$

which is then introduced into our β function (4.3) and "fixed point" expression (4.4a) to see if we obtain an expression that makes more intuitive sense. Inserting the definition (6.1) into (4.4a) implies that the fixed point for a surface (variable $d_\perp$) interacting chain with excluded volume can be written

$$u_{s,2}^* = \epsilon_\perp'/2 + \mathcal{O}(\epsilon^2,\epsilon_\perp'\epsilon) \tag{6.2}$$

and the β function in terms of (6.1) and (6.2) becomes after some simple algebra

$$\beta_s = (\epsilon_\perp'/2)u_{s,2}[1 - u_{s,2}/u_{s,2}^*] \tag{6.3}$$

Equations 6.3 and 6.2 reduce in an obvious way ($\epsilon_\perp' \to \epsilon_\perp$) to the exact results for Gaussian chains given in (4.3) and (4.4). Our results are now perfectly sensible. The peculiar $u_2/\epsilon_\perp$ term in (4.3) disappears, and spurious negative fixed points are not obtained *provided* we remain above the excluded volume-dependent critical dimension $1/\nu + d_\parallel$.

7. Theoretical Predictions

We are now in a position to make numerous concrete predictions of our proposed method, which can be tested

against Monte Carlo data and limiting cases solvable by standard methods.

Important dimensionless universal properties $\gamma_{\mathbf{R}_\perp}{}^2$ and $\gamma_{\mathbf{R}}{}^2$ [see (3.9)] characterizing the effect of the surface interaction for a terminally attached chain are given by[7]

$$\gamma_{\mathbf{R}_\perp}{}^2 = (1 - u_{s,2}{}^*)^{-1} + \mathcal{O}(\epsilon^2,\epsilon_\perp\epsilon) \tag{7.1}$$

$$\gamma_{\mathbf{R}}{}^2 = \langle \mathbf{R}^2\rangle / \langle \mathbf{R}^2\rangle_f = [d_\parallel + d_\perp/(1 - u_{s,2}{}^*)]/d + \mathcal{O}(\epsilon^2,\epsilon_\perp\epsilon) \tag{7.2}$$

where $u_s{}^*$ is defined by (6.2). The f subscript on $\langle \mathbf{R}^2\rangle_f$ indicates the "free chain" dimensions of a chain with excluded volume as above. (7.1) and (7.2) are expected to be quite accurate, however, and in fact are exact[7] for Gaussian chains ($z_2{}^\circ = 0$) and $\epsilon_\perp > 0$. Using the Flory value of $\nu = 3/(d + 2)$ for simplicity gives for the self-avoiding chain and repulsive surface limit:

$$\gamma_{\mathbf{R}}{}^2 = [d_\parallel + d_\perp/\{1 - [(d + 2)/3 + d_\parallel - d]/2\}]/d \tag{7.3}$$

and specializing to $d = 3$ and $d_\parallel = 2$, corresponding to a self-avoiding chain interacting with a plane, yields

$$\gamma_{\mathbf{R}}{}^2 = 7/6 \approx 1.17 \tag{7.4}$$

This is to be compared with earlier predictions using standard RG methods:[7,9]

$$\gamma_{\mathbf{R}}{}^2(z_2{}^\circ \to \infty, z_s{}^\circ \to \infty; \text{ penetrable surface}) = 1.20 \tag{7.5a}$$

$$\gamma_{\mathbf{R}}{}^2(z_2{}^\circ \to \infty, z_s{}^\circ \to \infty; \text{ impenetrable surface}) = 1.18 \tag{7.5b}$$

Setting $d_\parallel = 2$ in (6.2) and expanding to order ϵ imply

$$u_{s,2}{}^*(d_\parallel{=}2) = 3\epsilon/8 + \mathcal{O}(\epsilon^2) \tag{7.6}$$

which when inserted in (7.1) and (7.2) exactly recovers the results of Douglas et al.[7] for a surface interacting chain ($d_\parallel = 2$) with excluded volume. This is an important consistency check on our scheme.

The situation of a polymer interacting with a repulsive line ($d_\parallel = 1$) in three dimensions is also interesting. For Gaussian chains ($z_2{}^\circ = 0$), we have $u_{s,0}{}^* = \epsilon_\perp/2$, which *formally* vanishes in this instance. Actually, the approach to the noninteracting free-chain theory occurs rather slowly, and the crossover involves log corrections since we are at the critical dimension, i.e., $\phi_s{}^\circ = 0$. Douglas et al.[7] show that $\gamma_{\mathbf{R}_\perp}{}^2$ is equal (Gaussian chains, $d_\parallel = 1$; $d = 3$):

$$\gamma_{\mathbf{R}_\perp}{}^2 = 1 + z_s/[1 + z_s \ln (2\pi N/L)] + \mathcal{O}[\{z_s/[1 + z_s \ln (2\pi N/L)]\}^2] \tag{7.7}$$

where $z_s{}^\circ$ is a renormalized analogue of $z_s{}^\circ$, which must be introduced when working at the critical dimension. The $\perp$ subscript is regrettably omitted in ref 1 of Douglas et al.[7]

For chains with excluded volume ($\nu > {}^1/_2$) interacting with a line in three dimensions, the $\epsilon_\perp{}'$-parameter becomes negative, and this simply means that $\gamma_{\mathbf{R}}{}^2 = \gamma_{\mathbf{R}_\perp}{}^2 = 1$ *without* any log corrections. The situation is quite analogous to the case of a Gaussian chain (repulsion) interacting with a point where $\epsilon_\perp$ is formally negative [see (3.1a)] and where again $\gamma_{\mathbf{R}}{}^2 = \gamma_{\mathbf{R}_\perp}{}^2 = 1$. The larger the value of the *formally* obtained "negative fixed point", the more rapid an approach to free-chain behavior is expected. This can be seen by calculating $\gamma_{\mathbf{R}_\perp}{}^2$ from perturbation theory to obtain (Gaussian chains; $z_2 = 0$)

$$\gamma_{\mathbf{R}_\perp}{}^2 = 1 + (\text{const})z_s{}^\circ; \quad z_s{}^\circ \sim n^{\epsilon_\perp/2} \tag{7.8}$$

Instead of the slow log approach to free chain behavior, it is approached as a negative power law (proportional to $\epsilon_\perp$). For a Gaussian polymer interacting with a point in three dimensions, for example, we have

$$\gamma_{\mathbf{R}_\perp}{}^2 = 1 + (\text{const})n^{-1/2} \tag{7.9}$$

This result and (7.7) for large N are also given by Rubin in his lattice calculations.[1]

Finally, we remark that the situation of $d_\parallel = 1$ and $d = 3$ for a surface interacting chain with excluded volume is quite analogous to the problem of a polymer chain with *both* binary and ternary interactions.[18,19] In each case, we have two interactions with a critical dimension of 4 and 3, and the standard RG method can be applied as long as one of the interactions is restricted to be small (see Appendix B). As mentioned above, ternary interaction and surface interaction both give log corrections when the binary interaction vanishes. It is expected that as the chain swells (which has roughly the same effect as increasing the dimension of space because of a lower chain density), the ternary interaction becomes irrelevant. This would come about since the critical dimension of the ternary interaction should become *reduced* as found explicitly in the calculation above for the surface interacting chain with excluded volume. *No log corrections should then be found for swollen chains due to ternary interactions in $d = 3$.* It should be possible to extend the method described here to both binary and ternary interactions where *neither is restricted to be small.* However, it is prudent to first check the consistency of the proposed scheme to higher order for the simpler problem of a surface interacting polymer with excluded volume. By "simpler" we refer to the relative ease in which perturbation theory is calculated.

8. Conclusion

A renormalization group method is proposed for treating multiple interactions having differing critical dimensions. This method first involves a perturbation expansion in the surface and excluded volume interactions about the Gaussian reference state, which for vanishing excluded volume is just the usual two-parameter perturbation theory. Since the critical dimensions of the surface interacting Gaussian chain and the Gaussian chain with excluded volume are not the same, in general (they are for $d_\parallel = 2$, however), the perturbation expansion has poles in *both* $\epsilon_\perp = 2 + d_\parallel - d$ and $\epsilon = 4 - d$ (see Appendix C). This situation requires some kind of generalization (see Appendix D) of the standard method of renormalization. Here it is assumed that a *double expansion* in both $\epsilon_\perp$ and ϵ is appropriate for renormalizing the theory, and no difficulty is found working under this assumption to leading order. A redefinition of the $\epsilon_\perp$ parameter ($\epsilon_\perp{}'$) for the surface interaction is made based on scaling arguments for swollen surface interacting chains. Introduction of $\epsilon_\perp{}'$ leads to more readily interpretable results.

In summary, the excluded volume Gell-Mann–Low functions β_2 and Z_N are found to be unchanged (to leading order) from their "free chain" analogues. The β function and fixed point for the surface interaction within the multiple-ϵ renormalization scheme are equal:

$$\beta_s = (\epsilon_\perp{}'/2)u_{s,2}(1 - 2u_{s,2}/\epsilon_\perp{}') \tag{8.1a}$$

$$u_{s,2}{}^* = \epsilon_\perp{}'/2 + \mathcal{O}(\epsilon^2,\epsilon'\epsilon_\perp); \quad \epsilon_\perp{}' = 1/\nu + d_\parallel - d \tag{8.1b}$$

$$2\nu = 1 + u_2 + \mathcal{O}(\epsilon^2); \quad u_2{}^* = \epsilon/8 + \mathcal{O}(\epsilon^2) \tag{8.1c}$$

where the exponent ν is a function of the dimensionless excluded volume coupling constant u_2. For good solvents, ν can be reasonably approximated by the Flory value ν ($d = 3$) = ${}^3/_5$. The results (8.1a,b) are exact for Gaussian chains, and these results are also consistent with the results

obtained by Douglas et al.[7] for a special case ($d_\parallel = 2$) where the combined excluded volume and surface interactions can be treated without ambiguity.

Some of the numerous predictions of the multiple-ϵ theory are described and compared with previous calculations. The theoretical results are quite sensible, and the method is a promising approach for problems where multiple interactions and critical dimensions arise. In a polymer theory context, the most important potential application of the method is to the combined influence of both binary *and* ternary interactions,[18,19] where the binary interactions is not restricted to be small.

Finally, it is stressed that although the multiple-ϵ-expansion method presented here seems quite reasonable, the treatment to higher orders will certainly be quite difficult for a variety of reasons. The perturbation calculation is more involved, and the interpretation of d-dependent factors in terms of ϵ and $\epsilon_\perp$ parameters in a unique fashion is a delicate issue. Because of these anticipated difficulties and the additional *assumption of renormalizability*, the results of the scheme described here must be considered tentative until the higher order calculations are performed.

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Appendix A

The β function β_s is calculated through the standard relation[7]

$$\beta_s = L\frac{\partial}{\partial L}u_s(u_s^\circ, u_2^\circ) \tag{A.1}$$

where β_s°, β_2°, and N_0 are fixed as constants. The chain rule gives

$$\beta_s = L\frac{\partial}{\partial L}u_s^\circ\frac{\partial u_s}{\partial u_s^\circ} + L\frac{\partial}{\partial L}u_2^\circ\frac{\partial u_s}{\partial u_2^\circ} \tag{A.2}$$

and using the relations[7] [see (3.4)] $u_2^\circ \propto L^{\epsilon/2}$ and $\mu_s^\circ \propto L^{\epsilon_\perp/2}$ yields

$$\beta_s = (\epsilon_\perp/2)u_s^\circ\frac{\partial u_s}{\partial u_s^\circ} + (\epsilon/2)u_2^\circ\frac{\partial u_s}{\partial u_2^\circ} \tag{A.3}$$

Introducing the definition (3.5a) of the renormalization constant in (A.3) implies

$$\beta_s = (\epsilon_\perp/2)u_s[1 + u_s^\circ(\partial Z_{u_s}^{-1}/\partial u_s^\circ)/Z_{u_s}^{-1} + (\epsilon/\epsilon_\perp)u_2^\circ(\partial Z_{u_s}^{-1}/\partial u_2^\circ)/Z_{u_s}^{-1}] \tag{A.4}$$

and inserting (4.2) into (A.4) and expanding produce (4.3).

Appendix B

It is relatively easy to calculate the scaling functions for chains with excluded volume and surface interactions and variable surface dimension $d_\parallel$ provided one of the interactions is kept small. The procedure then parallels the approach to Θ point polymers[18,19] where the binary interaction is likewise *restricted to be small*. Only *one* ϵ-parameter arises in this circumstance.

Specifically, it is assumed that $z_2^\circ \sim \mathcal{O}(\epsilon_\perp)$ in the surface interaction problem, and it is also assumed that $d_\parallel \neq 2$ to avoid an "accidental degeneracy" $\epsilon_\perp = \epsilon$ occurring for $d_\parallel = 2$. In the treatment of ternary interactions it is similarly assumed[18,19] that the effective binary interaction (here denoted by z_2°) is on the order $z_2^\circ \sim \mathcal{O}(\epsilon_3)$, where $d = 3$ is the critical dimension of the ternary interaction and $\epsilon_3 = 3 - d$. Taking $d_\parallel = 1$ in the surface interaction model implies $\epsilon_\perp = \epsilon_3$ [see (2.4)], making the relation between the problems even more transparent.

The perturbation expansion for $\langle \mathbf{R}_\perp^2 \rangle$ in d-dimensions for a $d_\parallel$ dimension surface is given in (3.2). Taking $d_\parallel = 1$ restricts us to the regime $2 < d \leq 3$ since $\epsilon_\perp$ is negative for $d > 3$. Note that the expansion coefficient of z_2° is no longer singular in this range of d. Further, the restriction $z_2^\circ \sim \mathcal{O}(\epsilon_3)$ (i.e., small) allows us to take $Z_N = 1$. Introducing the renormalization constant Z_{u_s} into (3.3) gives [see (4.1)]

$$Z_{u_s} = 1 + 2u_s/\epsilon_\perp + \mathcal{O}(u_s^2); \quad z_2^\circ \sim \mathcal{O}(\epsilon_\perp) \tag{B.1}$$

which renormalizes the perturbation expansion for $\langle \mathbf{R}_\perp^2 \rangle$ under the rather narrow restriction of the near-Θ chains $z_2^\circ \sim \mathcal{O}(\epsilon_\perp)$ and $2 < d \leq 3$. The renormalization constant associated with z_2° is unity in leading order due to the lack of a singular cross term $z_2^\circ z_s^\circ$. To leading order, the renormalized perturbation theory for $\langle \mathbf{R}_\perp^2 \rangle$ [see (3.2)] is

$$\langle \mathbf{R}^2 \rangle = (d_\perp/d)\langle \mathbf{R}^2 \rangle_{0,f}[1 + C_{\mathbf{R}^2}(d)z_2^\circ + u_s + ...] \tag{B.2a}$$

$$C_{\mathbf{R}^2}(d) = [2/(4-d)]/[1 + (4-d)/2]; \quad C_{\mathbf{R}^2}(d=3) = 4/3 \tag{B.2b}$$

This is rewritten as [see (3.6b)]

$$\langle \mathbf{R}^2 \rangle = (d_\perp/d)\langle \mathbf{R}^2 \rangle_f/(1 - u_s) + \mathcal{O}(\epsilon_\perp^2) \tag{B.3a}$$

$$\langle \mathbf{R}^2 \rangle_f = \langle \mathbf{R}^2 \rangle_{0,f}[1 + C_{\mathbf{R}^2}(d)z_2^\circ + \mathcal{O}(\epsilon_2^2)]; \quad z_2^\circ \sim \mathcal{O}(\epsilon) \tag{B.3b}$$

where $\langle \mathbf{R}^2 \rangle_f$ denotes the free-chain dimensions with excluded volume.

The only nontrivial renormalization constant to leading order Z_{u_s} is the *same* as in the surface interacting Gaussian chain theory and the fixed point, and RG analysis to leading order in $\epsilon_\perp$ is then also identical. Thus we have a dimensionless coupling constant as defined in ref 7 as

$$u_s = u_{s,0}^*(z_s^\circ/u_{s,0}^*)/(1 + z_s^\circ/u_{s,0}^*); \quad u_{s,0}^* = \epsilon_\perp/2; \quad z_s^\circ \sim \mathcal{O}(\epsilon_\perp) \tag{B.4}$$

The scaling function for $\langle \mathbf{R}_\perp^2 \rangle$ is obtained by inserting (B.4) into (B.3a), yielding

$$\langle \mathbf{R}_\perp^2 \rangle = (d_\perp/d)\langle \mathbf{R}^2 \rangle_f[1 - u_{s,0}^*(z_s^\circ/u_s^*)/(1 + z_s^\circ/u_s^*)]^{-1} + \mathcal{O}(\epsilon_\perp^2); \quad z_2^\circ \sim \mathcal{O}(\epsilon_\perp) \tag{B.5}$$

where $\langle \mathbf{R}^2 \rangle_f$ is given by (B.3b).

In the special case of $d_\parallel = 2$, the average normal dimensions $\langle \mathbf{R}_\perp^2 \rangle$ can be calculated without difficulty[7] to leading order as

$$\langle \mathbf{R}_\perp^2 \rangle = (d_\perp/d)\langle \mathbf{R}^2 \rangle_f\left\{1 + u_s^*(z_2^\circ)\frac{z_s^\circ(1 + z_2^\circ/u_2^*)^{-1/4}/[u_s^*(z_2^\circ)]}{1 + z_s^\circ(1 + z_2^\circ/u_2^*)^{-1/4}/[u_s^*(z_2^\circ)]}\right\}^{-1} + \mathcal{O}(\epsilon^2) \tag{B.6}$$

where $\langle \mathbf{R}_\perp^2 \rangle$ and $\langle \mathbf{R}^2 \rangle_f$ are *not restricted to small excluded volume* and where the following definitions are employed:

$$u_s^*(z_2^\circ) = (\epsilon/2)(3\lambda_2/4)/[1 - (1 - \lambda_2)^{3/4}] \tag{B.7a}$$

$$\lambda_2 = (z_2^\circ/u_2^*)/(1 + z_2^\circ/u_2^*); \quad u_2^* = \epsilon/8 + \mathcal{O}(\epsilon^2) \tag{B.7b}$$

For vanishing $z_2°$ the excluded volume dependent fixed point $u_s^*(z_2°)$ approaches $u_{s,0}^*$ in (B.4) so that (B.6) and (B.5) are consistent in this limit.

The treatment of ternary and binary interactions is quite analogous to the case of combined surface and excluded volume. In terms of the binary $\hat{z}_2$ and ternary interaction variables z_3 (the circumflex indicates that the effective interaction is shifted by a ternary contribution)[18,19] the mean-square end-to-end vector distance is[18]

$$\langle \mathbf{R}^2 \rangle = \langle \mathbf{R}^2 \rangle_{0,f}[1 + C_{\mathbf{R}^2}(d)\hat{z}_2(1 + z_3°/u_3^*)^{-4/11} - 1.90u_3^*(z_3°/u_3^*)/(1 + z_3°/u_3^*)]; \quad \hat{z}_2 \sim \mathcal{O}(\epsilon_3) \quad \text{(B.8)}$$

where $\epsilon_3 = 3 - d$, $u_3^* = \epsilon_3/44\pi + C(\epsilon_3^2)$ and $d < 3$. The variables $\hat{z}_2(1 + z_3°/u_3^*)^{-4/11}$ and $z_3°/u_3^*$ are denoted as ρ and χ, respectively, in Cherayil et al.[17] log corrections are obtained as $d \to 3$ just as in (7.7). The correction term to z_2 with the $-4/11$ exponent in (B.8) arises from the nonsingular cross term $\hat{z}_2 z_3°/\epsilon_3$ in the perturbation expansion for $\langle \mathbf{R}^2 \rangle$ in $\hat{z}_2$ and $z_3°$, which is analogous to (3.3).

Appendix C

Another situation where there are two critical dimensions corresponds to a polymer interacting with a plane surface ($d_\parallel = 2$) having a line defect (a scratch, say) where the interaction strength on the *line defect* is different than the polymer–plane interaction. The Hamiltonian for this system is then

$$\mathcal{H}/K_BT = \mathcal{H}_0 + z_{s,plane}° \int_0^1 dx\ \delta[\mathbf{r}_\perp(x)](2\pi)^{(d-2)/2} + z_{s,line}° \int_0^1 dx\ \delta[\bar{\mathbf{r}}_\perp(x)](2\pi)^{(d-1)/2} \quad \text{(C.1)}$$

where $\mathbf{r}_\perp(x)$ and $\bar{\mathbf{r}}_\perp(x)$ are the projections of $\mathbf{r}(x)$ normal to the plane and line, respectively. The dimensionless interactions scale as

$$z_{s,line}° = (d/2\pi l^2)^{(d-1)/2}\beta_{s,line}° n^{(3-d)/2} \quad \text{(C.2a)}$$

$$z_{s,plane}° = (d/2\pi l^2)^{(d-2)/2}\beta_{s,plane}° n^{(4-d)/2} \quad \text{(C.2b)}$$

The critical dimensions for this model system are the same as for the combination of binary and ternary interactions. High-order ϵ-expansion calculations and exact calculations can be pursued to further check the multiple-ϵ perturbation scheme or any other proposed method of dealing with the problem of multiple-ϵ-parameters.

Appendix D

There is a conceivable (but necessarily long-winded and complicated) method of calculating the configuration properties of a Gaussian chain with a surface interaction (variable $d_\perp$) *and* excluded volume without introducing the multiple-ϵ method. This can be done by combining the method used by Nemirovsky and Freed[8] for the impenetrable surface problem and the method of Douglas et al.[7] The crux of the method is to exploit the *exact solvability* of the surface interaction chain model due to the one-body nature of the interaction potential and to use the surface interacting chain model as our unperturbed model. Thus, instead of $\mathcal{H}_0$ given by (2.1), our reference Hamiltonian $\mathcal{H}_{ref}$ is taken as[8,9] [see (2.1) and (2.2)]

$$\mathcal{H}°_{ref} = \mathcal{H}_0 + \mathcal{H}_s$$

which is a function of $\epsilon_\perp$. The excluded volume *alone* is added as a perturbation, and the perturbation theory is then renormalized in a standard fashion. Of course, this is a rather complicated perturbation calculation because the end-vector distribution function of the unperturbed reference theory becomes a complicated function of the surface interaction and $\epsilon_\perp$. In principle, the end-vector distribution function of surface interacting chain can be obtained following the methods of Douglas et al.,[7] who calculate some of its moments exactly for the full range of surface interaction. This provides another avenue for testing the multiple-ϵ approach introduced in this paper.

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(23) Fixman, M. *J. Chem. Phys.* **1955**, *23*, 1656. Edwards, S. F. *Proc. Phys. Soc.* **1965**, *85*, 613. See also Rubin in ref 10.
(24) Freed, K. F. *Renormalization Group Theory of Macromolecules*; Wiley: New York, 1987.
(25) In the multiple-ϵ method the perturbative parameters ϵ and $\epsilon_\perp$ do not necessarily vanish at the same critical dimension ($d_\parallel \neq 2$), and one of these parameters must be larger than the other. Some might object to this property since the perturbation scheme depends on the "smallness" of the ϵ-parameters. In fact, the smallness of ϵ is *required not* by mathematical principle but by the practical constraint of obtaining an accurate ϵ perturbative description at low order in the perturbation expansion. The multiple expansion is an acceptable mathematical scheme for counting powers in perturbation theory, but no doubt it will achieve the best accuracy under the condition that both ϵ and $\epsilon_\perp$ are small—not necessarily equal, however.
(26) Bray, A. J.; Moore, M. A. *J. Phys. A: Math. Gen.* **1977**, *10*, 1927.
(27) See Diehl and Dietrich in ref 5 and the following: Ohno, K.; Okabe, Y. *Prog. Theor. Phys.* **1983**, *70*, 1226.
(28) Nemirovsky, A. M.; Wang, Z.-G.; Freed, K. F. *Phys. Rev. B: Condens. Matter* **1986**, *34*, 7886.
(29) (a) Kremer, J. *J. Chem. Phys.* **1985**, *83*, 5882. (b) Ishinabe, T. *J. Chem. Phys.* **1983**, *80*, 1318. Monte Carlo simulations for the impenetrable surface are given by: Eisenriegler, E.; Kremer, K.; Binder, K. *J. Chem. Phys.* **1982**, *77*, 6298.
(30) (a) Hughes, B. D. *Physica A: (Amsterdam)* **1986**, *134A*, 443. If we relax the constraint that the mean-square step length of the random walk is finite, we are led to the study of the Lêvy flight random walks. Since the individual steps of the random walk can involve large jumps in the case when the mean-square step distance is not finite, the Lêvy flights tend to extend to greater distances in space than their simple random-walk analogues. Perhaps the most conspicuous property of Lêvy flights is that the exponent ν characterizing their average dimensions $R \sim n^\nu$ is larger than its Gaussian chain counterpart ν (Gaussian) = $^1/_2$. This situation is, of course, analogous to the effect of repulsive excluded volume. Hughes shows that a Lêvy flight does not necessarily return to the origin when the dimension is greater than $1/\nu$. The dimension $1/\nu$ defines the critical dimension of the Lêvy flight [see (d) below] interacting with a point that we see is continuously variable. In the paper we argue by analogy with the exactly solvable Lêvy flight model [see Darling and Kac[1]] and scaling arguments that the critical dimension of the surface interacting chain is a function of ν, with the variation of ν arising from the excluded volume interaction. (b) Gillis, J. E.; Weiss, G. *J. Math. Phys.* **1970**, *11*, 1307. (c) Seshadir, V.; West, B. J. *Proc. Natl. Acad. Sci. U. S.A.* **1982**, *79*, 4501. (d) A RG treatment of a Lêvy flight interacting with a point ($d_\parallel = 0$) by J.D. leads exactly to (5.4), (6.1), and (6.2), where ν_{LF} equals the reciprocal fractal dimension of the Lêvy flight. There is a slight difference in the Lêvy flight analogue of the Gell-Mann–Low β function of (6.3) where $\epsilon_\perp'/2$ is replaced by $\epsilon_\perp'\nu_{LF}$. For a continuum formulation of the Lêvy flight model with excluded volume see: Prentis, J. *J. Phys. A: Math. Gen.* **1985**, *18*, L833. See also ref 7. The Lêvy flight model provides an *exactly soluble* model where the critical dimension is explicitly a function of the chain density through the exponent ν as indicated in our perturbative multiple-ϵ-expansion calculations.
(31) Mandelbrot, B. *The Fractal Geometry of Nature*; Freeman: San Francisco, 1977.