Test of Renormalization Group Crossover Dependence: Comparison with Exact Solution for a Polymer Attached to a Penetrable Interacting Hypersurface

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ABSTRACT: The partition function, end-vector distance $\langle \mathbf{R}^2 \rangle$, and a variety of other properties are calculated for a Gaussian polymer in d dimensions which is terminally attached to a penetrable interacting hypersurface of dimensionality $d_\parallel$. Calculations for this model, originally introduced by Kosmas, are performed to all orders in the polymer–surface interaction and the perturbation expansions are resummed to provide *exact* closed-form solutions which are applicable over the whole crossover range (attractive and repulsive) of the polymer–surface interaction. These exact solutions are then compared with approximate renormalization group (RG) descriptions of the crossover which are deduced from the first couple of orders of the polymer–surface interaction perturbation expansion. The general shape of the crossover is rather well approximated in the *positive* interaction regime by the RG theory, but a singular behavior is found at a critical negative value of the surface interaction, corresponding to the collapse of the polymer onto the $d_\parallel$-dimension hypersurface. This occurs even though the model and the exact solution are well-defined in the negative interaction regime. The approximate RG crossover dependence of the polymer–surface interaction is shown to be very similar to that for the polymer–polymer excluded volume interaction. Insights gained by comparing the exact and approximate RG crossover for the surface interaction problem are very useful in understanding the more complicated crossover for polymer–polymer interactions where there are no exact solutions.

I. Introduction

The renormalization group (RG) method, in conjunction with the two-parameter (TP) model of polymer excluded volume, has been very successful in describing the excluded volume dependence of large length scale polymer properties above the Θ point.[1] However, this approach relies on the perturbative ϵ-expansion method whose success in treating crossover dependence has only been judged empirically through comparison between theory and experiment for a wide class of polymer properties.[1] It is of considerable interest to obtain an *independent* test of the adequacy of the crossover dependence predicted by the RG theory through a comparison with an exactly solvable nontrivial model.

Kosmas[2] has introduced an ideal model for such a comparison. This model considers the interaction of a polymer in d-dimensional space with a penetrable surface of continuously variable dimension $d_\parallel$. The crossover behavior of this model may be studied by use of RG expansions in the polymer–surface interaction along with expansions in $\epsilon_\perp = 2 - d_\perp$, where $d_\perp + d_\parallel = d$. In addition, we show that the perturbation expansion of the Kosmas model in the polymer–surface interaction may be evaluated to all orders for Gaussian chains and that the perturbation series can be resummed into closed analytic form. This provides the required exact crossover dependence of the polymer properties on the polymer–surface interaction for comparison with the approximate RG treatment truncated to low order in $\epsilon_\perp$. While the resummability of the perturbation expansion for the special case of $d_\parallel = d - 1$ is to be anticipated from the exact solvability of the model by alternative methods,[3] the general $d_\parallel$-dimensional model is nontrivial, providing the desired comparison to check the adequacy of RG descriptions of crossover behavior.

Our ability to calculate several polymer properties to all orders of the polymer–surface interaction with the Kosmas model for Gaussian chains indicates that this model is far simpler than the TP model of polymer–polymer interactions whose approximate RG crossover dependence we ultimately wish to assess. However, we show that the two crossover dependences have a similar analytic structure, and this suggests the applicability of some conclusions based on the Kosmas model to the polymer–polymer interaction problem.

The description of a polymer near an interacting penetrable surface is also of considerable interest in the study of polymers in the vicinity of liquid–liquid interfaces, of emulsion stabilization, and numerous other applications.[4] There have recently been Monte Carlo simulations by Ishinabe[5] and Kremer[6] for self-avoiding lattice polymers interacting with penetrable surfaces, and Hammersley et al.[7] have obtained exact analytical results for lattice random walks with penetrable and impenetrable surfaces. Although our primary interest lies in testing the accuracy of the RG description of crossover dependences, we also discuss some of the properties of Gaussian polymers at penetrable interfaces. A previous paper focuses on the impenetrable surface problem.[4]

The Kosmas model[2] is introduced in section II and is discussed in relation to the TP model of polymer excluded volume. The perturbation series in the polymer–surface interaction for the configurational partition function and the mean square end-vector distance $\langle \mathbf{R}^2 \rangle$ are then evaluated in section III to all orders for Gaussian chains with the Kosmas model. The perturbation expansions are shown to have an infinite radius of convergence for $\epsilon_\perp > 0$ and a zero radius of convergence for $\epsilon_\perp < 0$. First, a closed-form resummation of the perturbation expansion for the partition function is obtained for general $\epsilon_\perp$ in terms of the Mittag–Leffler function.[8] Second, the RG method is applied to the Kosmas model through the first few orders of the $\epsilon_\perp$ expansion in section IV. The approximate RG crossover dependence for $\langle \mathbf{R}^2 \rangle$ is then compared with the exact analytical solution for the convenient and physically most important case of $d_\parallel = d - 1$. Similarities are noted between polymer–polymer crossover behavior and that for the polymer–surface interaction. The RG description of the negative interaction regime is ill-behaved in both problems, and our exact solution for the negative (attractive) surface interaction regime is used to construct an approximate scheme for describing the full crossover. This scheme should also be useful in the construction of a theory of the polymer–polymer interaction over the full range of interactions. Further discussions of

0024-9297/86/2219-2207$01.50/0

other properties within the Kosmas model and of the order of the adsorption phase transition as a function of $d_\perp$ are given in Appendix A.

II. Model

The unperturbed model is a continuous Gaussian chain backbone which is perturbed by a δ-function pseudopotential for the polymer–surface interaction. Phenomenological parameters in this coarse-grained model are complicated functions of the detailed microscopic interactions. The hypothesis of universality, however, leads us to expect that the microscopic details can be subsumed into the scaling variables derived from a minimal model to obtain a universal description of large-scale properties.

The continuous chain model configuration is specified by the position vector $\mathbf{R}(x)$ of the chain segment at a contour distance x along a chain of length N_0. For convenience, the position vector $\mathbf{R}(x)$ is written in terms of reduced units of the mean square end-to-end distance $\langle \mathbf{R}^2 \rangle_{0,f}$ of a free unperturbed chain as

$$\mathbf{r}(x) = \mathbf{R}(x)[d/\langle \mathbf{R}^2 \rangle_{0,f}]^{1/2} \tag{2.1}$$

In these units the dimensionless configurational Hamiltonian for the polymer–surface interactions is

$$\mathcal{H}/k_B T = \mathcal{H}_0 + \mathcal{H}_s(\text{polymer–surface}) \tag{2.2a}$$

where the unperturbed portion

$$\mathcal{H}_0 = (1/2)\int_0^1 dx \left|\frac{d\mathbf{r}(x)}{dx}\right|^2 \tag{2.2b}$$

reflects chain connectivity and where $k_B T$ is the absolute temperature in energy units.

The interacting surface is a hypersurface of dimension $d_\parallel$ embedded in a space of dimensionality d. A vector $\mathbf{r}_\parallel(x)$ is defined as the projection of $\mathbf{r}(x)$ onto this surface, and $\mathbf{r}_\perp(x)$ is the projection onto an orthogonal space of dimension $d_\perp$. Within a representation similar to that introduced by Edwards[9] for the polymer–polymer excluded volume interaction, the surface interaction portion of the Hamiltonian equals[2]

$$\mathcal{H}_s(\text{polymer–surface}) = z_s^0 \int_0^1 dx\ \delta[\mathbf{r}_\perp(x)](2\pi)^{d_\perp/2} \tag{2.2c}$$

where the dimensionless polymer–surface interaction parameter z_s^0 is defined as

$$z_s^0 = (d/2\pi l^2)^{d_\perp/2}\beta_s^0 n_0^{\epsilon_\perp/2}, \qquad \epsilon_\perp = 2 - d_\perp \tag{2.2d}$$

Here β_s^0 is the polymer–surface binary cluster integral and $\delta[\mathbf{r}_\perp(x)]$ is a $d_\perp$-dimensional δ function. Short-range correlations, such as the constraint against immediate reversal in lattice chains and restrictions on bond angles, etc., in real polymers are as usual implicitly absorbed into the definition of the effective step length l. The number of statistical segments n_0 is related to the chain contour length N_0 and to the free Gaussian chain mean square end-vector distance $\langle \mathbf{R}^2 \rangle_{0,f}$ through the definitions

$$\langle \mathbf{R}^2 \rangle_{0,f} \equiv N_0 l \equiv n_0 l^2 \tag{2.2e}$$

There is a very close formal similarity between the polymer–polymer and polymer–surface interaction perturbation series and also between the scaling functions, obtained after renormalization in these two models. Hence, we conclude this section by defining the interaction energy for the former problem to facilitate comparisons which are made in section IV. The polymer–polymer interaction contribution to the Hamiltonian is modeled by[4,9]

$$\mathcal{H}_2(\text{polymer–polymer}) = (z_2^0/2)\int_0^1 dx \int_0^1 dx'\,(2\pi)^{d/2}\delta[\mathbf{r}(x) - \mathbf{r}(x')] \tag{2.3a}$$

where z_2^0 of the two-parameter (TP) theory has the traditional polymer theory definition ($\epsilon = 4 - d$)

$$z_2^0 = (d/2\pi l^2)^{d/2}\beta_2^0 n_0^{\epsilon/2} \tag{2.3b}$$

with β_2^0 the polymer–polymer binary cluster integral. For $d_\parallel = 2$ we have $\epsilon_\perp = \epsilon$, which is the special case necessarily considered with the RG theory when both excluded volume and the surface interaction are present.[2,4]

III. Perturbative Calculation and Exact Resummation

Two basic approaches have appeared for treating the surface interaction model described in the previous section. The interaction potential in (2.2c) is a one-body potential, and the fixed end-vector partition function can be shown to satisfy a linear diffusion equation which is exactly solvable by classical methods for solving partial differential equations.[10] This diffusion equation approach has been reviewed by many authors[4,10,11] and has been mostly limited to the case $d_\perp = 1$. However, nothing in principle prevents the treatment of more general values of $d_\perp \in (0,d)$. For instance, Pincus et al.[12] and de Gennes[10] have considered the problems of adsorption (attractive interaction) onto a sphere, cylinder, and plane for $d = 3$ (see also ref 13).

Another procedure, introduced by Kosmas,[2] is to perturbatively expand the surface interaction in the same manner as in the standard TP model of polymer–polymer excluded volume. The unperturbed state, which is analogous to the Θ point for the polymer–polymer interaction, is that of a free Gaussian chain. In this section we perform the perturbation calculation through infinite order in the surface interaction parameter. After a resummation of the perturbation theory into closed form, the result obtained from the diffusion equation approach is recovered as a special case for $d_\perp = 1$. More generally, the perturbative expansion provides an exact solution for arbitrary $d_\perp$, although the convergence of the perturbation series requires $d_\perp \leq 2$.

A. Perturbative Calculation of $\langle \mathbf{R}^2 \rangle$. The end-vector distribution function $G(\mathbf{r},z_s^0)$ for a Gaussian chain with *one end attached to the wall* at $\mathbf{r} = 0$ is defined in terms of the model Hamiltonian $\mathcal{H}$ of (2.2) by

$$G(\mathbf{r},z_s^0) = \int_{\mathbf{r}(0)=0}^{\mathbf{r}(1)=\mathbf{r}} \mathcal{D}\{\mathbf{r}(x)\}\exp[-\mathcal{H}(z_s^0)/k_B T] \tag{3.1}$$

where $\mathcal{D}\{\mathbf{r}(x)\}$ is the Wiener conformational measure. This distribution function $G(\mathbf{r},z_s^0)$ can be Taylor-expanded around $G^0(\mathbf{r})$ for a free Gaussian chain. The familiar Gaussian propagator $G^0(\mathbf{r})$ has the form

$$G^0[\mathbf{r}(x)] = (2\pi x)^{-d/2}\exp(-r^2/2x) \tag{3.2}$$

Using the relation $|\mathbf{r}|^2 = r^2 = |\mathbf{r}_\parallel|^2 + |\mathbf{r}_\perp|^2$ implies that eq 3.2 can be factored to obtain

$$G^0[\mathbf{r}(x)] = G_\parallel^0[\mathbf{r}_\parallel(x)]G_\perp^0[\mathbf{r}_\perp(x)] \tag{3.3a}$$

such that

$$G_\parallel^0[\mathbf{r}_\parallel(x)] = (2\pi x)^{-d_\parallel/2}\exp(-\mathbf{r}_\parallel^2/2x) \tag{3.3b}$$

and

$$G_\perp^0[\mathbf{r}_\perp(x)] = (2\pi x)^{-d_\perp/2}\exp(-\mathbf{r}_\perp^2/2x) \tag{3.3c}$$

In the Kosmas approach[2] the surface interaction part of

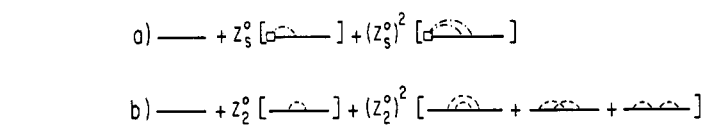

Figure 1. The free Gaussian chain propagator G^0 is denoted by a straight solid line, the polymer–surface interaction (a) by a dashed line ending at a box, and the polymer–polymer interaction (b) by a simple dashed line. The box is representative of the surface. In higher order in the excluded volume interaction there is a rapid proliferation[25] in the number of diagrams for the polymer–polymer interaction, and the diagrams for $\langle \mathbf{R}^2 \rangle_f$ through fifth order, for example, are given by Muthukumar and Nickel.[45] Only "ladder type" diagrams[46] arise in the z_s^0 expansion where there is a succession of embedded loops as in the first term of the second-order expansion of z_2^0. We speculate that the convergence of the surface interaction perturbation expansion and the stability of the fixed point ($u_s^* = \epsilon_\perp/2$) and exponents such as γ (see Appendix A) are associated with the absence of "meshed" loops which, in turn, is associated with the one-body nature of the interaction. For m-body excluded volume interactions ($m > 1$) and ϵ expansions for the fixed points and exponents generically have an asymptotic form[21] similar to (C.4), and this factorial growth in the ϵ-expansion coefficients seems to be associated with the combinatorics of distinguishable interaction vertices (see ref 25).

the Hamiltonian $\mathcal{H}$ in the exponential of (3.1) is perturbatively expanded to express $G(\mathbf{r},z_s^0)$ in power series in z_s^0, leading formally to

$$G(\mathbf{r}_\perp,\mathbf{r}_\parallel,z_s^0) = \int_{\mathbf{r}(0)=0}^{\mathbf{r}(1)=\mathbf{r}} \mathcal{D}\{\mathbf{r}(x)\} \exp(-\mathcal{H}_0) \times \left(1 - \mathcal{H}_s + \frac{1}{2!}\mathcal{H}_s^2 + \dots\right), \qquad z_s^0 \ll 1 \quad (3.4a)$$

or explicitly from (2.2) this gives

$$G(\mathbf{r}_\perp,\mathbf{r}_\parallel,z_s^0) = G_\parallel^0(\mathbf{r}_\parallel)[G_\perp^0(\mathbf{r}_\perp) - z_s^0 \int_0^1 dx\, (2\pi)^{d_\perp/2} G_\perp^0(\mathbf{0},x) G_\perp^0(\mathbf{r}_\perp,1-x) + (z_s^0)^2 \int_0^1 dx' \int_0^{x'} dx\, (2\pi)^{d_\perp} G_\perp^0(\mathbf{0},x) G_\perp^0(\mathbf{0},x'-x) G_\perp^0(\mathbf{r}_\perp,1-x') + \mathcal{O}[(z_s^0)^3] \quad (3.4b)$$

Equation 3.4b is still separable into two parts

$$G(\mathbf{r}_\perp,\mathbf{r}_\parallel,z_s^0) = G_\parallel^0(\mathbf{r}_\parallel) G_\perp(\mathbf{r}_\perp,z_s^0) \quad (3.4c)$$

leaving the parallel component $G_\parallel^0(\mathbf{r}_\parallel)$ unaffected by the surface interaction.

The expansion (3.4b) is diagrammatically depicted in Figure 1a and is contrasted with that for the polymer–polymer excluded volume interaction which is given in Figure 1b. To stress the comparison with the TP theory the first-order expansion[4,14] for $G(\mathbf{r},z_2^0)$ for a free chain is

$$G(\mathbf{r},z_2^0) = G^0(\mathbf{r}) - z_2^0 \int_0^1 dx'\,(1-x')(2\pi)^{d/2} G^0(\mathbf{0},x') G^0(\mathbf{r},1-x') + \mathcal{O}[(z_2^0)^2] \quad (3.5)$$

The leading contributions to the polymer–polymer and polymer–surface perturbative expansions are identical for $d = d_\perp$ in (3.4b) and (3.5), aside from the factor of $(1 - x')$ in (3.5) (see Appendix A) coming from an iterated integral and from an interchange of interaction labels.

One of the basic quantities derivable from the distribution function $G(\mathbf{r},z_s^0)$ is the partition function Q, defined as

$$Q(z_s^0,\epsilon_\perp) = \int d^d\mathbf{r}\; G(\mathbf{r},z_s^0)$$

or explicitly from (3.4) and (3.3) as

$$Q(z_s^0,\epsilon_\perp) = 1 - z_s^0 \int_0^1 dx\, x^{-d_\perp/2} + (z_s^0)^2 \int_0^1 dx' \int_0^{x'} dx\, x^{-d_\perp/2}(x'-x)^{-d_\perp/2} + \mathcal{O}[(z_s^0)^3]$$

Through all orders in perturbation theory a terminally attached chain yields the series

$$Q(z_s^0,\epsilon_\perp) = \sum_{k=0}^{\infty} [-z_s^0 \Gamma(\epsilon_\perp/2)]^k / \Gamma(1 + k\epsilon_\perp/2) \quad (3.6)$$

where $\epsilon_\perp = 2 - d_\perp$ is defined in (2.2d) and Γ denotes the gamma function. The zero of free energy is chosen such that the partition function Q of the unperturbed chain ($z_s^0 = 0$) is unity. Equation 3.6 is generally termed a "bare" perturbation series as opposed to the resummed ("renormalized") theory introduced in section IV. The fact that the surface interaction is modeled by a one-body δ-function pseudopotential reduces the computational complexity and enables the perturbation theory to be obtained through infinite order [see (3.6) and (3.7e) below].

The end-to-end vector distance $\langle \mathbf{R}^2 \rangle$ is an important polymer property for characterizing the polymer configuration even though it is not a direct observable. It is also one of the simplest properties to calculate, so we focus on $\langle \mathbf{R}^2 \rangle$ as an illustrative example. It is convenient to calculate the $\langle \mathbf{R}_\parallel^2 \rangle$ and $\langle \mathbf{R}_\perp^2 \rangle$ components of $\langle \mathbf{R}^2 \rangle$ separately where these are the projections of $\langle \mathbf{R}^2 \rangle$ onto the $d_\parallel$- and $d_\perp$-dimension subspaces

$$\langle \mathbf{R}^2 \rangle = \langle \mathbf{R}_\parallel^2 \rangle + \langle \mathbf{R}_\perp^2 \rangle \quad (3.7a)$$

Equation 3.4c implies that the parallel component is unaffected by the surface interaction, so that it is the same as that for the free chain

$$\langle \mathbf{R}_\parallel^2 \rangle = (d_\parallel/d)\langle \mathbf{R}^2 \rangle_{0,f} \quad (3.7b)$$

Equation 3.7b is obviously not correct for a strong attractive interaction ($z_s^0 \to -\infty$), where $\langle \mathbf{R}_\parallel^2 \rangle$ must approach $\langle \mathbf{R}^2 \rangle_{0,f}$ independent of dimention ($d_\parallel \geq 1$) because this limit produces a random walk in the $d_\parallel$-dimension space. The deficiency of (3.7b) arises since the dimensionality of space, which the polymer "senses", is a *function* of the interaction. This effective dimension $d(z_s^0)$ has the physically clear limits $d(z_s^0 \to -\infty) = d_\parallel$ and $d(z_s^0 \geq 0) = d$. A correct model can, in principle, be derived from lattice random walk calculations where, for instance, Rubin[7] finds $\langle \mathbf{R}_\parallel^2 \rangle$ depends on the surface interaction in a model-specific fashion. It still remains to derive the appropriate continuum-limit model in the attractive interaction regime. However, since (3.7b) does describe a dimensional crossover from a d-dimensional random walk for $z_s^0 \geq 0$ to a $d_\parallel$-dimensional-like one for $z_s^0 \to -\infty$, we continue to use it as a vehicle for studying the accuracy of the RG theory for crossover dependences of polymer properties on the polymer–surface interaction.

The perpendicular component $\langle \mathbf{R}_\perp^2 \rangle$ is computed from (3.3) and (3.4a) as

$$\langle \mathbf{R}_\perp^2 \rangle = (1/d)\langle \mathbf{R}^2 \rangle_{0,f} \int d^d\mathbf{r}\; \mathbf{r}^2 G(\mathbf{r}_\perp,\mathbf{r}_\parallel;z_s^0) / \int d^d\mathbf{r}\; G(\mathbf{r}_\perp,\mathbf{r}_\parallel;z_s^0) \quad (3.7c)$$

After integrating out the parallel component in (3.7c), we find

$$\langle \mathbf{R}_\perp^2 \rangle = \langle \mathbf{R}^2 \rangle_{0,f}(1/d) \int d^{d_\perp}\mathbf{r}_\perp \mathbf{r}_\perp^2 G_\perp(\mathbf{r}_\perp,z_s^0)/Q \quad (3.7d)$$

Proceeding in the same fashion as in the case of Q, the perturbation expansion for $\langle \mathbf{R}_\perp^2 \rangle$ through all orders is

$$\langle \mathbf{R}_\perp{}^2 \rangle = (d_\perp/d)\langle \mathbf{R}^2 \rangle_{0,f}\{\sum_{n=0}^{\infty}(-1)^n[z_s{}^0\Gamma(\epsilon_\perp/2)]^n/\Gamma(2+n\epsilon_\perp/2)\}/Q \quad (3.7e)$$

withe Q given by (3.6) and where (3.7e) corresponds to a terminally attached chain.

Many properties of relevance to a polymer interacting with a penetrable surface are readily evaluated in this manner. Appendix A compiles several of the more important properties besides (3.6) and (3.7e). The main point of our work, however, is the comparison with the perturbative RG solutions, and (3.6) and (3.7e) suffice for this because the other properties in Appendix A exhibit similar characteristics.

Next we show that Q, for example, can be written in terms of the Mittag–Leffler function,[15] whose properties are described in detail by Hardy.[8] This enables us easily to derive asymptotic expansions in the limits of large positive and negative surface interactions for arbitrary $\epsilon_\perp$. A specialized discussion is provided for $d_\perp = 1$, since a comparison can be made in this case with exact solutions from the diffusion equation approach and since the crossover function is considerably simpler for $d_\perp = 1$. In the following section we apply the RG through the first few orders of $\epsilon_\perp$ perturbation theory and compare the RG crossover dependence with the exact solution for $d_\perp = 1$ and with certain limits for general $\epsilon_\perp$.

B. Exact Resummation of the Surface Interaction Perturbation Theory. First, it is useful to make some basic observations about the perturbation series (3.6) and (3.7e). The ratio test implies that the radius of convergence of the perturbation series is infinite for $\epsilon_\perp > 0$. Furthermore, when $\epsilon_\perp = 1$, the perturbation expansions are expressible in terms of simple hypergeometric functions. For example, eq 13.1.3, 3.1.2, and 13.6.39 of Abramowitz and Stegun[16] enable the transformation of (3.6) into

$$Q(z_s{}^0,\epsilon_\perp = 1) = \exp\{[\Gamma(1/2)z_s{}^0]^2\}\ \mathrm{erfc}\ [\Gamma(1/2)z_s{}^0] \quad (3.8)$$

where erfc is the error function complement. The moment $\langle \mathbf{R}_\perp{}^2 \rangle$ is found from (3.7e) in the same way to be ($d_\perp = 1$)

$$\langle \mathbf{R}_\perp{}^2 \rangle = \langle \mathbf{R}^2 \rangle_{0,f}(d_\perp/d)\{\exp[\Gamma(1/2)z_s{}^0]\ \mathrm{erfc}\ [\Gamma(1/2)z_s{}^0] + 2\Gamma(1/2)z_s{}^0/\pi^{1/2} - 1\}/Q \quad (3.9)$$

The relatively simple analytic forms of (3.8) and (3.9) make these crossover functions convenient for our comparison with our RG calculations below.

The case of $\epsilon_\perp \neq 1$ also allows for a closed-form expression for Q and related properties, although the resulting functions are more complicated. Equation 3.6 defines the series for the Mittag–Leffler[8,15] function

$$Q = E_{\epsilon_\perp/2}[-z_s{}^0\Gamma(\epsilon_\perp/2)]$$

which is discussed on p 198 of ref 8. Following Hardy,[8] the partition function Q in the large-$z_s{}^0$ limit may be shown to have the asymptotic series (assuming $0 \leq \epsilon_\perp \leq 4$ and $\epsilon_\perp \neq 2$ unless otherwise noted) given by

$$Q \sim (-1)\sum_{k=1}^{\infty}[-z_s{}^0\Gamma(\epsilon_\perp/2)]^{-k}/\Gamma(1-k\epsilon_\perp/2) = 1/z_s{}^0\Gamma(\epsilon_\perp/2)\Gamma(1-\epsilon_\perp/2) + \mathcal{O}[(z_s{}^0)^{-2}] \quad (3.10)$$

When $z_s{}^0 \to -\infty$, the partition function Q exhibits a nonanalytic stretched exponential behavior[8]

$$Q \sim (2/\epsilon_\perp)\exp\{[-z_s{}^0\Gamma(\epsilon_\perp/2)]^{2/\epsilon_\perp}\}, \qquad z_s{}^0 \to -\infty \quad (3.11)$$

Generalizing the argument given by Hardy[8] we compute $\langle \mathbf{R}_\perp{}^2 \rangle$ in the $z_s{}^0 \to \infty$ limit to obtain

$$\langle \mathbf{R}_\perp{}^2 \rangle \sim [(d_\perp\langle \mathbf{R}^2 \rangle_{0,f}/d)/(1-\epsilon_\perp/2)]g(z_s{}^0) \quad (3.12a)$$

or

$$\langle \mathbf{R}_\perp{}^2 \rangle \sim (2\langle \mathbf{R}^2 \rangle_{0,f}/d)g(z_s{}^0) \quad (3.12b)$$

where

$$g(z_s{}^0) = 1 - (\epsilon_\perp/2)\Gamma(1-\epsilon_\perp/2)/z_s{}^0\Gamma(\epsilon_\perp/2)\Gamma(2-\epsilon_\perp) + \mathcal{O}[(z_s{}^0)^{-2}], \qquad z_s{}^0 \to \infty \quad (3.12c)$$

For the opposite limit of $z_s{}^0 \to -\infty$ we find

$$\langle \mathbf{R}_\perp{}^2 \rangle \sim (d_\perp\langle \mathbf{R}^2 \rangle_{0,f}/d)[-z_s{}^0\Gamma(\epsilon_\perp/2)]^{-2/\epsilon_\perp}, \qquad z_s{}^0 \to -\infty \quad (3.13)$$

A simple calculation shows that these limits are recovered from (3.8) and (3.9) for the special case of $d_\perp = 1$. The novel behavior of Q for $\epsilon_\perp < 0$ and $\epsilon_\perp > 4$ is discussed in Appendix B.

The exact resummation of the perturbation series in terms of known functions thus enables us to describe the nonanalytic limiting behavior of the perturbation theory in closed form. It is simple with hindsight to understand the scaling behavior in (3.11) and (3.13). The argument of the exponential in (3.11) is just the free energy of the polymer relative to the noninteracting free-chain limit (see Appendix A). Since almost all of the polymer is adsorbed onto the surface in the $z_s{}^0 \to -\infty$ limit, this change in free energy must be proportional to n_0 *independent of dimension*. This result, in turn, implies the free energy is proportional to $(z_s{}^0)^{2/\epsilon_\perp}$. Similarly, eq 3.13 can be understood physically as just a statement that the layer thickness of the strongly adsorbed isolated polymer is independent of molecular weight. Equation 3.12a and the crossover dependence in (3.9) are compared below with the predictions of the RG theory.

IV. Renormalization Group Treatment of Crossover in Polymer–Surface Interaction

There are a limited number of nontrivial statistical mechanical models which can be solved exactly and which exhibit phase transitions. The polymer–surface interaction model is a valuable example because much can be learned about the RG method and its limitations by applying the RG procedure to this exactly solvable model. The RG description of the polymer–surface interaction closely parallels that given previously for the polymer–polymer interaction,[1] and below we discuss some of their similarities and differences.

A. End-to-End Distance $\langle \mathbf{R}^2 \rangle$. The perturbative RG manipulation of $\langle \mathbf{R}_\perp{}^2 \rangle$ begins by rewriting (3.7e) explicitly in $z_s{}^0$ as

$$\langle \mathbf{R}_\perp{}^2 \rangle = [d_\perp\langle \mathbf{R}^2 \rangle_{0,f}/d][1 - (2z_s{}^0/\epsilon_\perp)/(1+\epsilon_\perp/2) + (2z_s{}^0/\epsilon_\perp)^2\Gamma^2(1+\epsilon_\perp/2)/\Gamma(2+\epsilon_\perp) + ...]/[1 - (2z_s{}^0\epsilon_\perp) + (2z_s{}^0/\epsilon_\perp)^2\Gamma^2(1+\epsilon_\perp/2)/\Gamma(1+\epsilon_\perp) + ...] \quad (4.1)$$

Expanding the denominator in (4.1) then gives the $z_s{}^0$ perturbation expansion

$$\langle \mathbf{R}_\perp{}^2 \rangle = \langle \mathbf{R}^2 \rangle_{0,f}(d_\perp/d) \times \{1 + z_s{}^0[1/(1+\epsilon_\perp/2) - (2/\epsilon_\perp)z_s{}^0/(1+\epsilon_\perp/2)(1+\epsilon_\perp) + (2/\epsilon_\perp)^2(z_s{}^0)^2/(1+\epsilon_\perp)(1+3\epsilon_\perp/2)] + \mathcal{O}[(z_s{}^0)^4]\} \quad (4.2)$$

There are evidently formal poles in $\epsilon_\perp$ associated with the $(z_s{}^0)^2$ and higher order terms in (4.2). These poles contain information on how the perturbation theory is to be resummed, and this information is extracted through the introduction of renormalization constants. The first step

in this procedure is the definition of a dimensionless "coupling constant" u_s^0 to provide a dimensionless measure of the polymer–surface interaction. A coarse-graining interaction length scale L_s and the quantity u_s^0 are introduced in the alternate definition of z_s^0

$$z_s^0 \equiv u_s^0(2\pi N_0/L_s)^{\epsilon_\perp/2} \tag{4.3}$$

The $\epsilon_\perp$ expansion for $\langle \mathbf{R}_\perp^2 \rangle$ is then obtained by expanding all terms in $\epsilon_\perp$, apart from the poles in $(\epsilon_\perp)^{-n}$, in a Taylor series in $\epsilon_\perp$.

The RG procedure next involves introducing a renormalization constant Z_{u_s} (u_s is termed the "renormalized coupling constant") defined by

$$u_s^0 = u_s Z_{u_s} = u_s(1 + a_1 u_s/\epsilon_\perp + a_2 u_s^2/\epsilon_\perp^2 + ...) \tag{4.4a}$$

into the definition of z_s^0 in (4.3). Then (4.4a) is substituted into the $\epsilon_\perp$-expanded form of (4.2), and the unknown constants $a_1, a_2, ...$ are determined such that all the $\epsilon_\perp$ poles in the resultant perturbation expansion of $\langle \mathbf{R}_\perp^2 \rangle$ in both u_s and $\epsilon_\perp$ vanish identically. Applying this recipe, Z_{u_s} is found as

$$Z_{u_s} = 1 + (2u_s/\epsilon_\perp) + (2u_s/\epsilon_\perp)^2 + ... \tag{4.4b}$$

The general case which includes the polymer–polymer interactions also has a renormalization constant Z_N defined by

$$Z_N^{-1} N = N_0 \tag{4.4c}$$

where Z_N is responsible for a change in the exponent ν of $\langle \mathbf{R}^2 \rangle \propto n_0^{2\nu} l^2$ from its Gaussian value of $\nu_0 = {}^1/_2$. The exact solution (3.13) and the perturbation expansion (4.1) both imply that $Z_N = 1$ when polymer–polymer interactions are absent. When excluded volume is introduced into the model, Z_N is no longer equal to unity, and this more general case will be discussed elsewhere.[17]

After extraction of the poles, the renormalized perturbation series is computed from (4.2) and (4.4) as

$$\langle \mathbf{R}_\perp^2 \rangle = (d_\perp/d)\langle \mathbf{R}^2 \rangle_{0,f}\{1 + u_s(2\pi N/L_s)^{u_s+\epsilon_\perp/2}[1 - (\epsilon_\perp/2) + 2u_s] + \mathcal{O}(\epsilon_\perp^3)\} \tag{4.5}$$

where the usual reexponentiation of terms in $\ln(2\pi N/L_s)$ has been made. The RG equation is now introduced to convert perturbative result (4.5) for small u_s into a full description of the crossover dependence of $\langle \mathbf{R}_\perp^2 \rangle$.

B. RG Crossover Analysis. We now summarize some of the basic results of the RG crossover analysis which permit the extraction of the global analytic structure of the exact solution from the apparently meager information contained in the first couple or orders of the polymer–surface interaction perturbation theory. For a detailed account of this interpretation of the RG analysis the reader is referred to ref 1.

$\langle \mathbf{R}_\perp^2 \rangle$ with a surface interaction is described by the scaling function

$$\langle \mathbf{R}_\perp^2 \rangle = f[L_s^{-\epsilon_\perp/2} u_s^0 = L_s^{-\epsilon_\perp/2}(u_s Z_{u_s}); 2\pi N_0] \tag{4.6a}$$

which upon scaling gives

$$\langle \mathbf{R}_\perp^2 \rangle = \langle \mathbf{R}^2 \rangle_{0,f} f(z_s^0) \tag{4.6b}$$

where z_s^0 is defined by (4.3). The RG equation is obtained by differentiating (4.6a) with respect to L_s where the arguments $L_s^{-\epsilon_\perp/2} u_s^0$ and N_0 are *fixed*. Noting that $Z_N = 1$ for a Gaussian chain and that $L_s^{-\epsilon_\perp/2} u_s^0$ is independent of L_s, this leads to the simple RG equation

$$\left(L_s \frac{\partial}{\partial L_s} + \beta_s \frac{\partial}{\partial u_s} \right)_F f = 0 \tag{4.6c}$$

where the Gell-Mann–Low β function is defined by

$$\beta_s(u_s) = L_s \left.\frac{\partial u_s}{\partial L_s}\right|_F = L_s \left.\frac{\partial u_s^0}{\partial L_s}\right|_F \frac{\partial u_s}{\partial u_s^0} = (\epsilon_\perp/2) u_s^0 \frac{\partial u_s}{\partial u_s^0} \tag{4.6d}$$

and the F subscript indicates differentiation with the arguments of f in (4.6a) held fixed.

It is easily verified upon direct substitution that (4.6c) has the solution

$$\langle \mathbf{R}_\perp^2 \rangle = f\left\{ L_s^{-\epsilon_\perp/2} \exp\left[(\epsilon_\perp/2) \int_{u_s^*/2}^{u_s} dx/\beta_s(x) \right]; 2\pi N_0 \right\} \tag{4.6e}$$

where u_s^* is the nontrivial root of $\beta_s(u_s)$ (see below for the definition of u_s^*) and where the lower limit $u_s^*/2$ in (4.6e) is chosen as a matter of convenience. Scaling lengths in (4.6e) by $\langle \mathbf{R}_\perp^2 \rangle$ in the $z_s^0 = 0$ limit, i.e., by $\langle \mathbf{R}_\perp^2 \rangle [z_s^0 = 0] = (d_\perp \langle \mathbf{R}^2 \rangle_{0,f}/d) \propto N_0$, we obtain

$$\langle \mathbf{R}_\perp^2 \rangle = (d_\perp \langle \mathbf{R}^2 \rangle_{0,f}/d) f(\zeta_s) \tag{4.6f}$$

where the scaling variable ζ_s of the renormalized theory is defined as

$$\zeta_s = (2\pi N_0/L_s)^{\epsilon_\perp/2} \exp\left[(\epsilon_\perp/2) \int_{u_s^*/2}^{u_s} dx/\beta_s(x) \right] \tag{4.7a}$$

An explicit form of ζ_s is obtained by first determining $\beta_s(u_s)$. Inserting (4.4b) into (4.6c) gives to second order in u_s

$$[\beta_s(u_s)/u_s^*]/(\epsilon_\perp/2)u_s = 1 - \bar{u}_s + \mathcal{O}(\bar{u}_s^3) \tag{4.8a}$$

$$\bar{u}_s = u_s/u_s^*; \qquad u_s^* = \epsilon_\perp/2 + \mathcal{O}(\epsilon_\perp^3) \tag{4.8b}$$

It is very likely that (4.8a) and (4.8b) hold to all orders in perturbation theory. Combining (4.7a) and (4.8a) yields

$$\zeta_s = (2\pi N_0/L_s)^{\epsilon_\perp/2} \bar{u}_s/(1 - \bar{u}_s) + \mathcal{O}(\epsilon_\perp^3) \tag{4.7b}$$

The renormalized perturbation expansion in (4.5b) is made consistent with the requirements of the RG equation by inverting (4.7b) to generate the function $u_s(\zeta_s, N_0/L_s)$, which is to be inserted into (4.5b). In first and second order in $\epsilon_\perp$ eq 4.7b is inverted, respectively, as

$$u_s = u_s^* \zeta_s/(1 + \zeta_s) + \mathcal{O}(\epsilon_\perp^2) \tag{4.7c}$$

$$u_s = u_s^*[\zeta_s/(1 + \zeta_s)](2\pi N_0/L_s)^{-\epsilon_\perp/2(1+\zeta_s)} + \mathcal{O}(\epsilon_\perp^3) \tag{4.7d}$$

Substituting (4.7c) and (4.7d) into (4.5b) gives

$$\langle \mathbf{R}_\perp^2 \rangle = (d_\perp/d)\langle \mathbf{R}^2 \rangle_{0,f}[1 + u_s^* \lambda_s + \mathcal{O}(\epsilon_\perp^2)], \qquad u_s^* = \epsilon_\perp/2 + \mathcal{O}(\epsilon_\perp^2) \tag{4.9a}$$

$$\langle \mathbf{R}_\perp^2 \rangle = (d_\perp/d)\langle \mathbf{R}^2 \rangle_{0,f}[1 + u_s^* \lambda_s + (u_s^*)^2(2\lambda_s^2 - \lambda_s) + \mathcal{O}(\epsilon_\perp^3)], \qquad u_s^* = \epsilon_\perp/2 + \mathcal{O}(\epsilon_\perp^3) \tag{4.9b}$$

where λ_s is an abbreviation for

$$\lambda_s = \zeta_s/(1 + \zeta_s) \tag{4.8c}$$

Equations 4.9a and 4.9b are central RG expressions, which we now proceed to compare with *exact* results for $\epsilon_\perp = 1$.

The strong surface interaction limit of $\zeta_s \to \infty$ simplifies (4.9b) to

$$\langle \mathbf{R}_\perp^2 \rangle = (d_\perp/d)\langle \mathbf{R}^2 \rangle_{0,f}[1 + \epsilon_\perp/2 + (\epsilon_\perp/2)^2 + \mathcal{O}(\epsilon_\perp^3)], \qquad z_s^0 \to \infty \tag{4.9c}$$

which is equal to the expansion of the exact result (3.12) to second order in $\epsilon_\perp$. We observe that the prefactor coefficient in square brackets in (4.9c) appears to converge as a geometric sequence (see Appendix C).

In order to compare the $\epsilon_\perp$-perturbative RG solution and the exact solution, it is necessary to determine the relation between the renormalized crossover variable ζ_s and the

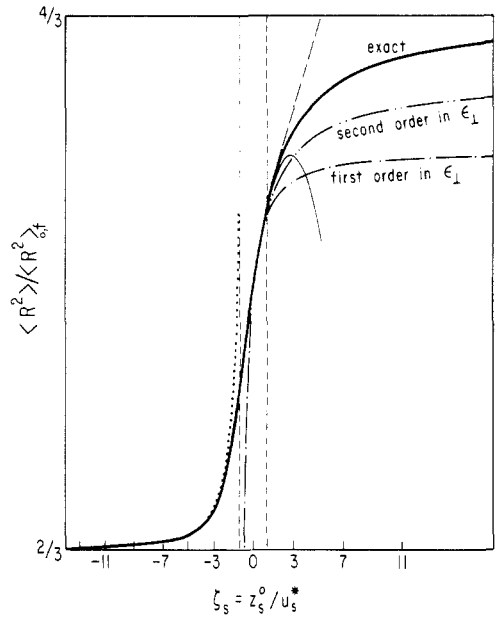

Figure 2. Our exact solution for $\langle \mathbf{R}^2 \rangle$ is denoted by the dark solid line, and the first and second order in $\epsilon_\perp$ calculations are denoted by dashed–dot and dashed–double dot lines, respectively. The thin solid line is a second-order Taylor expansion, and the long dashed line is a third-order Taylor expansion. The asymptotic ground-state-dominant solution for large negative z_s^0 is represented by a dotted line. Short vertical dashed lines denote the fixed-point values of the interaction $z_s^0 = \pm u_s^*$, enclosing the regime in which the first-order Taylor expansion (a linear perturbation) holds to a good approximation. A similar splitting pattern for $z_2^0 \approx u_2^*(d = 3) \approx 0.1$ is evident in Figure III.4 of Yamakawa[24] for the two-parameter perturbation expansion. In ref 18 the limit $z_2^0 \to -u_2^*$ has been identified with the onset of the coil–globule transition, and in this figure we see that the limit $z_s^0 \to -u_s^*$ corresponds to a sharp crossover to the adsorbed polymer state. See the discussion after eq 3.7b which explains a difficulty with the continuum model in the attractive interaction regime.

bare variable z_s^0. This relation is frequently not considered in RG calculations but is easily determined as follows: Equation 4.6 provides the definition

$$\partial \ln [(u_s^0)^{2/\epsilon_\perp}]/\partial u_s \equiv 1/\beta_s(u_s) \tag{4.10a}$$

which implies that

$$u_s^0/u_s^* \equiv \bar{u}_s Z_{u_s}\{\bar{u}_s\} = \exp\left[(\epsilon_\perp/2)\int_{u_s^*/2}^{u_s} dx/\beta_s(x)\right] \tag{4.10b}$$

Thus, by definition ζ_s and Z_{u_s} are equal to

$$\zeta_s = z_s^0/u_s^* \tag{4.7e}$$

$$Z_{u_s} = (1 - \bar{u}_s)^{-1} + \mathcal{O}(\bar{u}_s^3) \tag{4.11}$$

Expanding (4.11) in powers of $\bar{u}_s$ recovers (4.4b) as it must. Consequently, a *main point of the RG crossover scaling analysis is to obtain a resummed form of these renormalization constants.* Knowledge of the resummed renormalization constants then enables the analytic continuation of the low-order perturbation theory out of the perturbative regime $|z_s^0| \le u_s^*$.

We now come to a central point of our paper, namely, the evaluation of the $\epsilon_\perp$-expansion error in the first couple of orders of the $\epsilon_\perp$-perturbation theory. This error can be visualized from Figure 2, where the first and second order in $\epsilon_\perp$ RG predictions (4.9) are compared with the exact solution (3.9) for $\epsilon_\perp = 1$. The overall shape of the scaling function is rather well reproduced by the RG predictions in the range $z_s^0 \in (-u_s^*, \infty)$. To first order in $\epsilon_\perp$ the RG theory in the strong repulsive interaction limit ($z_s^0 \to \infty$) gives a 14% error for $\langle \mathbf{R}^2 \rangle$, while in second order the error is 7% relative to the exact solution for $\epsilon_\perp = 1$.

Figure 2 exhibits a splitting pattern for successive orders of the bare (unrenormalized) perturbation theory as $z_s^0 \to u_s^*$ where the different orders deviate for $z_s^0 > u_s^*$. A similar splitting of the bare perturbation theory occurs for $z_s^0 \to -u_s^*$ but is not depicted to avoid clutter. Since the perturbation theory has an infinite radius of convergence, the truncated bare perturbation expansion (4.2) eventually settles down to accurately approximating the exact scaling function if a sufficiently large number of terms are kept in (4.2). Figure 2, however, indicates that the fixed point u_s^* has the interpretation as the range of the polymer–surface interaction at which the first-order (linear approximation) perturbation theory is a good approximation, and $|z_s^0| \le u_s^*$ generally prescribes the range in which low-order perturbation theory is to be trusted. The RG ϵ-expansion method evidently proceeds by resumming infinite sub-sequences of the polymer–surface interaction perturbation theory to obtain an increasingly global perturbative description of the full solution from the locally restricted ($z_s^0 \le u_s^*$) truncated Taylor expansion. The convergence of the perturbation expansions for the surface interaction problem appears to be uniform in the positive interaction regime [see (4.9c) and (3.12a)].

C. Region of Negative z_s^0. Whereas the model and exact solutions are well-defined for $z_s^0 < 0$, it is frustrating that the chain space Gell-Mann–Low RG theory, in its present form, does not permit the description of the negative interaction regime because of its intrinsically singular behavior as the dimensionless interaction z_s^0 approaches its negative fixed-point value $-u_s^*$. All of the analytic information for the full range of the polymer–surface interaction is contained in the original polymer–surface interaction perturbation expansions (3.6) and (3.7e), and it may be hoped that *some* perturbative method exists for treating the negative interaction regime. The failure of the standard RG procedure in the negative interaction regime also indicates that under certain circumstances the standard RG theory *cannot be trusted.* Hence, there is a need for criteria to recognize these situations and for the development of methods which extend the RG theory into the negative interaction regime for the treatment of numerous problems in polymer physics where there are attractive interactions. Such a description is relevant to the coil–globule transition,[18] the collapse of blocks within block copolymers,[19,20] and the polymer coexistence curve as well as the adsorption of polymers onto surfaces. We cannot give a full solution to this very basic problem, but we do provide several observations to help in understanding the failure of the RG theory in the negative interaction regime and we suggest a method for treating the whole positive and negative range of interaction. Those readers more interested in how the comparison in subsection B bears on the expected accuracy of the RG crossover for polymer–polymer interactions may skip to subsection D below.

At a purely mathematical level the RG theory through (4.8c) defines a mapping between the positive real axis and the interval [0,1]. The original perturbation expansion in z_s^0/u_s^* [see (3.6)] is simply reexpressed as an expansion in the new variable λ_s. The transformed expansion in low order in λ_s provides a better global approximation to the exact solution than the starting perturbation expansion in z_s^0/u_s^*. The transformation (4.8c) is, in fact, the Euler (E,q) summation method[8] in which the q parameter of the general Euler transform is effectively optimized in a specific way ($q = 1/u_s^*$) by the RG theory.

Hardy[8] notes that the Borel resummation method may be regarded as the $q \to \infty$ limiting case of Euler summa-

tion, so that we can learn something about the limitations of RG resummation from the well-known limitations of the Borel method. The analytic continuation of Borel-transformed series is typically confined to a half-plane,[8] just as is our RG treatment of the surface interaction. Further, a common signature for a series which is not Borel summable[9] is a nonalternation in signs of the coefficients of the series.[21] Equation 4.1 for negative z_s^0 is of this latter form with all coefficients *positive*. Another signature[21] of series with nonalternating coefficients is the existence of a limiting nonanalytic behavior which is not readily extracted from perturbation expansions, a behavior displayed in (3.11) and (3.13). This leads to the general conclusion that the RG method in its present form should be applied with caution for bare perturbation expansions with nonalternating coefficients.

Another approach to the negative interaction regime involves expanding about the limiting dimensionally reduced state where the polymer is adsorbed strongly onto the $d_\parallel$-dimension hypersurface. The diffusion equation with δ-function polymer–surface pseudopotential only has a single bound state (i.e., discrete eigenvalue), so this approach corresponds to the usual "ground-state-dominant" (gsd) approximation.[10-12] For an impenetrable plane surface de Gennes[8] gives the gsd end-vector distribution $G^\perp_{gsd}$ as (see Appendix A for the case of general $\epsilon_\perp$)

$$G^\perp_{gsd} = \exp[-2^{1/2}\Gamma(1/2)z_s^0|\mathbf{r}_\perp|], \qquad d_\perp = 1 \tag{4.12}$$

which upon explicit calculation of $\langle \mathbf{R}^2 \rangle$ for a terminally attached Gaussian chain yields

$$\langle \mathbf{R}^2 \rangle = (d_\parallel \langle \mathbf{R}^2 \rangle_{0,f}/d)\{1 + (4/d_\parallel\pi)/(-z_s^0/u_s^*)^2 + \mathcal{O}[(-z_s^0/u_s^*)^{-3}]\}, \qquad z_s^0 \to -\infty, \quad d_\perp = 1 \tag{4.13}$$

This leading contribution is denoted by a dotted line in Figure 2 and is identical for $z_s^0 \to -\infty$ to the prediction of (3.13) for $d_\perp = 1$. Figure 2 shows that the gsd contribution accurately approximates the exact solution well up to point where $z_s^0 \approx -u_s^*$ from below. Nemirovsky and Freed[22] have introduced an effective Hamiltonian scheme in which the gsd term is the leading contribution. This allows for the calculation of fluctuations which become important as $z_s^0 \to -u_s^*$.

There is a simple physical reason for the divergence in the gsd theory as $z_s^0 \to -u_s^*$. The free energy of the adsorbed polymer [see (3.11) and Appendix A] is given by

$$\langle \mathcal{H}_s \rangle_{gsd} \propto E_0 n_0 = |-z_s^0\Gamma(\epsilon_\perp/2)|^{2/\epsilon_\perp}, \qquad z_s^0 \to -\infty \tag{4.14}$$

where E_0 is the free energy per monomer unit in the adsorbed state. E_0 also is the eigenvalue of the diffusion equation for the gsd mode. (See Appendix A.) A strongly adsorbed chain corresponds to E_0 on the order of unity, but as $z_s^0 \to -u_s^*$ the gsd eigenvalue E_0 approaches zero as $E_0 \sim 1/n_0 \to 0$, and the desorption transition occurs. In this limit the gsd mode ceases to give the dominant contribution.

Figure 2 shows that a rather good approximation to the exact crossover function for all z_s^0 can be constructed separately in three different regimes. First, the RG constructs an approximation for $z_s^0 > 0$ from a low-order perturbation expansion. The negative interaction regime is well represented by the gsd theory for $z_s^0 < -u_s^*$. Lastly, the bare perturbation theory provides a good approximation in the "linear" regime $|z_s^0| \leq u_s^*$, so that perturbation theory can be applied in the remaining regime $z_s^0 \in (-u_s^*, 0)$. We believe that a similar method should provide a workable approach for a variety of more complicated problems, such as polymer collapse, where no exact solution for comparison is possible.

D. Comparison between the ϵ Expansions for Crossovers in the Polymer–Polymer and Polymer–Surface Interactions. The description of the crossover dependence of dimensionless polymer properties on the polymer–polymer excluded volume interaction is very similar to that of the polymer–surface interaction. For example, Oono and Freed[23] give the first order in ϵ crossover scaling function for the ratio of the end-vector distance to the radius of gyration of a free chain

$$\langle \mathbf{R}^2 \rangle / 6\langle S^2 \rangle = 1 + (u_2^*/12)\lambda_2 + \mathcal{O}[(u_2^*\lambda_2)^2] \tag{4.15a}$$

$$\epsilon = 4 - d \qquad u_2^* = \epsilon/8 + \mathcal{O}(\epsilon^2)$$
$$\lambda_2 = \zeta/(1 + \zeta) \tag{4.15b}$$

Here ζ is the "renormalized" excluded volume scaling variable analogous to ζ_s for the polymer–surface interaction. Douglas and Freed[1] show that $\zeta \equiv z_2^0/u_s^*$, which is analogous to (4.7e), and they provide numerous other ratios which are based upon available TP theory perturbation calculations.

There are many parallels between the polymer–surface and polymer–polymer interaction problems besides the obvious resemblance of (4.9b) and (4.18a). The same characteristic splitting pattern for successive orders of perturbation theory, which is also found for $|z_s^0| \approx u_s^*$ in Figure 2, is present in Figure III.4 of Yamakawa[24] for $z_2^0 \approx u_2^* \sim \mathcal{O}(0.1)$ for $d = 3$. Again we see that u_2^* specifies the range in which the perturbation theory is to be trusted. This explains why in the past it was though the polymer–polymer excluded volume interaction had a finite radius of convergence,[24] $|z_2^0| \leq 0.15$. Although these perturbation series generically have a zero radius of convergence,[25,26] the range $|z_2^0| \leq u_2^*$ specifies the "range of utility" of these asymptotic series (see Appendix C).

Strictly, of course, the model (2.3) is not defined for $z_2^0 < 0$, but by introducing an infinitesimal ternary interaction z_3^0 the TP model can be extended into the attractive interaction regime.[18] Given this extension to negative z_2^0, it is found[18] that the RG description of the polymer–surface interaction and the polymer–polymer interaction problem becomes unphysically singular as the dimensionless interaction parameter approaches the negative value of its fixed point, i.e., $z_2^0 \to -u_2^*$. Elsewhere[18] we have identified the $z_2^0 \to -u_2^*$ limit with the incipient coil–globule transition, and the validity of this identification is clear in the case of the polymer–surface transition (see Figure 2) where comparison can be made with the exact solution. Our comparison with the experimental data of Perzynski et al.[18,27] indicates that the limit $z_2^0 \to -u_2^*$ coincides reasonably well with the collapse transition for radius of gyration and intrinsic viscosity.

Given this strong analogy between the polymer–polymer and polymer–surface interaction problems, it is tempting to conjecture that the free energy of the collapsed polymer is dominated by a term of the form [see (A.10)]

$$\langle \mathcal{H}_2 \rangle_{collapse} \propto E_0 n_0 = |-z_2^0/u_2^*|^{2/\epsilon} \tag{4.16}$$

corresponding to the gsd mode in the polymer collapse problem. Lattice data in support of this hypothesis are given by Ishinabe,[29] who attributes a relation similar to (4.16) to Moore.[30] Inserting this ansatz for E_0 into the theory developed by Moore[30] and by Kholodenko and Freed[28] gives rise to a picture of the polymer collapse problem which is very similar to that for the collapse of a polymer onto a surface. Very importantly, (4.16) implies that the coil–globule transition occurs for $z_2^0 \to -u_2^*$ in the gsd theory. The combination of the gsd mode theory (the mean field theory[28]) for the poor solvent regime, perturbation theory from the Θ regime, and the RG theory for

the good solvent regime offers the prospect of a comprehensive description of polymer properties over the whole range of the excluded volume interaction. Essentially this same program was suggested by Moore.[36] The effect of fluctuations can also be calculated by using the Kholodenko and Freed[28] theory, just as the recent work of Nemirovsky and Freed[22] includes fluctuations for the polymer–surface transition.

So far we have stressed similarities between the polymer–polymer and polymer–surface interaction problems. However, the perturbation expansions in ϵ such as (4.15a) are generally expected to be *asymptotic* rather than convergent (see Appendix C). This is a consequence of the likely asymptotic nature of the original perturbation theory in z_2^0. The best we can expect from the RG theory is then an extension of the "range of utility" of the perturbation theory from $|z_2^0| \leq u_2^*$ to $z_2^0 \gg u_2^*$. It is then necessary to treat the polymer–polymer perturbation expansions in ϵ differently than (4.9). The lack of uniform convergence for these series implies that the results do not necessarily improve upon calculating higher order terms in ϵ. Another important difference between the polymer–polymer and polymer–surface interaction problems is that it is difficult to obtain more than just the first couple of terms in the perturbation expansion for measurable polymer properties. A standard way of treating this type of series, when there is such limited information, is by determining the "optimal order of truncation" to obtain the best approximation. The philosophy of this procedure is described by Bender and Orzag,[31] and a discussion of the optimal order of truncation for the polymer–polymer interaction is described in Appendix C.

V. Conclusion

The perturbation series for a Gaussian polymer interacting with a penetrable surface is calculated within the Kosmas model[2] to all orders in the polymer–surface interaction. The series is exactly resummed for the general case of a $d_\parallel$-dimensional hypersurface embedded in a d-dimensional space. Renormalization group ϵ-expansion methods are then applied to perturbatively resum the surface interaction perturbation theory in powers of $\epsilon_\perp = 2 - d_\perp$. The renormalization group predictions are compared with the exact results for strongly repulsive surfaces, and in this limit there are 14 and 7% errors, respectively, in first and second order in the $\epsilon_\perp$-perturbation theory for the mean square end-vector distance $\langle \mathbf{R}^2 \rangle$ of a terminally attached chain. The convergence of the $\epsilon_\perp$ expansion is uniform in higher orders. An increasingly accurate expression is predicted by the renormalization group theory for the crossover function describing variable *repulsive* polymer–surface interactions, and the convergence appears again to be uniform.

Our renormalization group solution, however, is found to break down as the dimensionless polymer–surface interaction approaches $z_s^0 \to -u_s^* = -\epsilon_\perp/2$ from above. Another scheme is introduced for the large negative interaction regime which approximates the end-vector distribution function by the ground-state-dominant contribution. This method is found to give a good approximation for negative z_s^0 up to the limit $z_s^0 \to -u_s^*$ from below. An approximate description of the full crossover is obtained by patching together these complementary approaches.

We then describe the close similarity between the crossover dependence in the polymer–polymer excluded volume problem and that of the polymer–surface interaction problem. The renormalization group analysis is virtually identical in both cases aside from a change of interaction labels. Both the polymer–surface and polymer–polymer interaction problems exhibit a singular behavior as the interaction approaches its negative fixed-point value. These similarities make the Kosmas model a useful probe into the RG description of the polymer–polymer interaction.

Acknowledgment. This work is partially supported by NSF Grant DMR-83-18560. J.F.D. gratefully acknowledges the support of an IBM Fellowship. We also thank Professor Kosmas for sending us his work prior to publication.

Appendix A: Other Selected Properties for a Polymer Attached to a Penetrable Interacting Surface ($z_2^0 = 0$)

The main body of the paper compares exact expressions for $\langle \mathbf{R}^2 \rangle$ and Q with approximate RG predictions to gauge purely mathematical questions regarding the accuracy of $\epsilon_\perp$-expansion perturbation theory for the crossover in z_s^0. The general theory of a polymer interacting with a hypersurface is also a model of some physical significance. Thus, we consider a selection of properties for this system, including a discussion of the order of the adsorption transition.

1. Average Surface Interaction Free Energy Change $\langle \mathcal{H}_s \rangle$. The Θ state for polymer–polymer interactions in Monte Carlo simulations and in direct enumeration calculations of lattice polymers is defined as a critical value of the nearest-neighbor interaction at which $\langle \mathbf{R}^2 \rangle$ is proportional to n_0 or at which the second virial coefficient vanishes. These conditions have no direct analogue for the polymer–surface interaction. Usually the adsorption theta point Θ_A, where the effective surface interaction z_s^0 vanishes, is determined in simulations from the fraction of adsorbed monomer units which vanishes[4,32] asymptotically for $T > \Theta_A$ and $n_0 \to \infty$. Alternatively, Θ_A is deduced from properties such as the average surface interaction energy per monomer unit which likewise vanishes for $T > \Theta_A$ in the $n_0 \to \infty$ limit (see ref 4 for a discussion).

The average free energy change, due to polymer–surface interactions and relative to that for a noninteracting chain, is easily calculated from the partition function Q (one end attached to surface) as

$$\langle \mathcal{H}_s \rangle = \left\langle z_s^0 \int_0^1 dx\ \delta[\mathbf{r}_\perp(x)] \right\rangle = -\partial \ln Q/\partial \ln z_s^0 \qquad \text{(A.1)}$$

Equation A.1 is evaluated from (3.6) by differentiating term by term to obtain

$$\langle \mathcal{H}_s \rangle = \sum_{k=0}^{\infty} [-z_s^0 \Gamma(\epsilon_\perp/2)]^k (-k)/[\Gamma(1 + k\epsilon_\perp/2)Q] \qquad \text{(A.2)}$$

A simple closed form for the average free energy change relative to a free polymer is then found from (3.8) for $d_\perp = 1$ as

$$\langle \mathcal{H}_s \rangle = 2(z_s^0/Q)\{1 - [\Gamma(1/2)z_s^0]^2(Q/z_s^0)\} \qquad \text{(A.3)}$$

while from (A.2) we have the limiting situations for $\epsilon_\perp \in (0,4)$ and $\epsilon_\perp \neq 2$:

$$\langle \mathcal{H}_s \rangle \sim 1, \qquad z_s^0 \to \infty \qquad \text{(A.4a)}$$

$$\langle \mathcal{H}_s \rangle \sim z_s^0/u_s^*, \qquad z_s^0 \to 0 \qquad \text{(A.4b)}$$

$$\langle \mathcal{H}_s \rangle \sim (-u_s^*)[-z_s^0 \Gamma(\epsilon_\perp/2)]^{2/\epsilon_\perp}, \qquad z_s^0 \to -\infty \qquad \text{(A.4c)}$$

The RG theory, on the other hand, yields in first order in $\epsilon_\perp$

$$\langle \mathcal{H}_s \rangle = \lambda_s \qquad \text{(A.5)}$$

which approaches the correct limits in (A.4a) and (A.4b)

but which fails as usual in the negative interaction regime since it becomes singular as $z_s^0 \to -u_s^*$.

The qualitative behavior of (A.4a–c) is easy to interpret. For large z_s^0 the average free energy change $\langle \mathcal{H}_s \rangle$ saturates and approaches a constant since only a finite number of segments are at the surface. In the opposite limit of $z_s^0 \to -\infty$ we must have $\langle \mathcal{H}_s \rangle \propto n_0$, independent of dimension, since most of the polymer is absorbed onto the hypersurface.

The limits $z_s^0 \to \infty$ and $z_s^0 \to -\infty$ are physically rather obvious, but the limit $z_s^0 \to 0$ is more subtle physically and provides insight into the nature of the polymer–surface interaction and into the order of the surface adsorption phase transition. From (2.2d) and (A.4b) we have

$$\langle \mathcal{H}_s \rangle \sim n_0^{\epsilon_\perp/2}, \qquad z_s^0 \to 0, \qquad \epsilon_\perp > 0 \tag{A.6}$$

This result arises because a very long polymer has a number of intersections with an arbitrarily drawn $d_\parallel$-dimension hypersurface (noninteracting) which scales according to (2.2d) and (A.4b) as $n_0^{\epsilon_\perp/2}$ for $\epsilon_\perp > 0$, while for $\epsilon_\perp < 0$ the intersection set has measure zero. In the language of Mandelbrot[33] the crossover exponent $\epsilon_\perp/2$ defines the fractal dimension of the set of intersection points.

There is also an important connection between the surface interaction crossover exponent and the problem of return probabilities in the theory of lattice random walks.[34] The probability that an infinite random walk strikes an arbitrary hypersurface of dimension $d_\parallel$ is no longer unity for $\epsilon_\perp < 0$. For example, it is well-known that the probability of return of an infinite lattice random walk to a point is not certain in $d = 3$ but rather is a nonuniversal probability less than unity. The probability of a random walk returning to a line in four dimensions should likewise be a probability less than unity, although the problem apparently has not been studied before. In the next subsection we discuss the bearing that the surface interaction exponent has on the order of the surface adsorption phase transition.

2. Order of the Surface Adsorption Transition. The order of the surface phase transition for the "collapse" of the polymer onto the surface is determined as the lowest order discontinuous temperature derivative of the free energy. The free energy per monomer unit $\langle \mathcal{H}_s \rangle / n_0$ of an adsorbed infinite chain scales according to (A.4c) as

$$\langle \mathcal{H}_s \rangle / n_0 \propto (\beta_s^0)^{2/\epsilon_\perp} \tag{A.7a}$$

In the vicinity of the transition point it is expected (see ref 4) that very long chains have the dependence[4]

$$\beta_s^0 \approx T - \Theta_A, \qquad \Theta_A/T \approx 1 \tag{A.7b}$$

where Θ_A is the adsorption Θ temperature ($z_s^0 = 0$) and T is the absolute temperature. Of course, the transition temperature and Θ_A do not coincide[4,32] for finite chains.[4] Adopting the Riemann–Liouville definition[35] of differentiation, where the order of differentiation is an arbitrary real number, then the order of the surface transition becomes $2/\epsilon_\perp$ in a generalized Ehrenfest sense.[36] The adsorption onto a plane and adsorption onto a line in three dimensions are thus second- and infinite-order phase transitions, respectively. Birshstein[37] and Gorbunov et al.[38] arrive at the same conclusion for $d = 3$ based upon lattice model calculations.

We can also make some qualitative remarks regarding how the order of the adsorption phase transition is altered by the presence of polymer–polymer excluded volume, by surface irregularity, and by the presence of finite boundaries. First, since $d_\perp > 0$, the order of the adsorption phase transition for Gaussian chains onto a $d_\parallel$-dimension hypersurface is greater than unity. Qualitatively, we then expect that for $d_\perp > 1$ the adsorption onto the "outside" of a large material object tends to be a continuous (second order or higher) transition. An increase in the irregularity of the hypersurface can be viewed as roughly equivalent to increasing $d_\parallel$ (increasing $\epsilon_\perp$ and decreasing the order of the transition) if we naively identify the variable $d_\parallel$ with the fractal dimension[33] of the adsorbing surface. For example, the fractal dimension of a Gaussian chain is $d_f = 2$; hence if $d_\parallel$ is chosen as $d_\parallel = d_f$, then $\epsilon_\perp$ becomes $\epsilon_\perp \equiv \epsilon = 4 - d$. Thus, in our naive picture of adsorption onto fractals the intermolecular polymer–polymer excluded volume interaction can be thought of a polymer interacting with a surface where the polymer is its own "surface". The crossover exponent $\epsilon/2$ then governs the probability of the self-intersections of the polymer. (This geometric interpretation for the polymer–polymer excluded volume interaction is discussed precisely in ref 39.) The qualitative effect of surface irregularity is thus to increase the sharpness of the adsorption phase transition relative to the idealized limiting Euclidean surface. Our qualitative discussion may also have some relevance to gel permeation chromatography where the adsorbent is rather irregular.[40]

Scaling arguments may be used to qualitatively assess the effect of excluded volume on the surface transition order. If (2.2c) were scaled by the *perturbed* chain size $\langle \mathbf{R}^2 \rangle_f$ of a free chain rather the unperturbed length $\langle \mathbf{R}^2 \rangle_{0,f}$, the dimensionless chain variable becomes $\hat{\mathbf{r}} = (d/\langle \mathbf{R}_f \rangle^2)^{1/2}\mathbf{R}$ and the dimensionless surface-interaction has the form

$$\begin{aligned} \mathcal{H}_s &= z_s^* \int_0^1 \delta[\hat{\mathbf{r}}_\perp(x)]\, dx (2\pi)^{d_\perp/2} \\ z_s^* &= (d/2\pi)^{d_\perp/2} \beta_s^0 n_0 / \langle \mathbf{R}^2 \rangle_f^{d_\perp/2} \end{aligned} \tag{A.8a}$$

In good solvents, where $\langle \mathbf{R}^2 \rangle_f \sim n_0^{2\nu}$, eq A.8a suggests that the good solvent surface crossover exponent ϕ_s^*, defined by $z_s^* \sim n^{\phi_s^*}$, equals

$$\phi_s^* = 1 - d_\perp \nu \tag{A.8b}$$

Equation A.8b corresponds to the Bray–Moore conjecture and to an argument by de Gennes in the special case of $d_\perp = 1$ (see ref 6). Equation A.8 is not expected to be exact since it fails to consider the "renormalization" of the chain contour length. Rather than a technical argument based upon the RG analysis we present the following heuristic argument for this effect: Alternatively (A.8a) can be written as

$$\mathcal{H}_s = \langle \mathbf{R}^2 \rangle_f^{-d_\perp/2} (d/2\pi)^{d_\perp/2} (\beta_s^0/l^2) \int_0^a d\tau'\, \delta[\hat{\mathbf{r}}_\perp(\tau')] \times (2\pi)^{d_\perp/2}, \qquad a = \langle \mathbf{R}^2 \rangle_{0,f}/l \tag{A.8c}$$

Replacing $\langle \mathbf{R}^2 \rangle_{0,f}$ by its perturbed value $\langle \mathbf{R}^2 \rangle_f$ gives

$$\mathcal{H}_s = (d/2\pi)^{d_\perp/2} (\beta_s^0/l^2) \langle \mathbf{R}^2 \rangle_f^{1-d_\perp/2} \int_0^1 dx'\, \delta[\hat{\mathbf{r}}_\perp(x')] (2\pi)^{d_\perp/2} \tag{A.8d}$$

For good solvents (z_2^0 large) eq A.8d yields

$$\phi_s^* = \epsilon_\perp \nu \tag{A.9}$$

Equations A.8b and A.9 *likely* provide lower and upper bounds on ϕ_s^*. Monte Carlo data seem to be in good accord[6] with (A.8b) for the penetrable surface and with (A.9) for the impenetrable surface[32] where $d_\perp = 1$. Our first-order RG calculations[17] for the penetrable surface ($d_\parallel = 2$) is in agreement with (A.8b); i.e., $\phi_s^* = 3\epsilon/8 + \mathcal{O}(\epsilon^2)$.

Physically the free energy change for an adsorbed polymer should scale as $\langle \mathcal{H}_s \rangle \propto n_0$, which implies that the

polymer is predominantly adsorbed on the hypersurface. This conclusion should be independent of whether or not there is excluded volume and of the detailed shape of the surface. For the many generalizations of the adsorption of polymer onto surfaces of different types we obtain different scaling variables $\hat{z}_s^0$ characterized by crossover exponents ϕ_s which are affected by the particular interactions which we include in our model and by the particular type of surface (surface curvature, penetrability, etc.). Since $\langle \mathcal{H}_s \rangle / n_0$ approaches a constant independent of dimension in the strongly adsorbed limit, we must have

$$\langle \mathcal{H}_s \rangle / n_0 \sim (\hat{z}_s^0)^{1/\phi_s}/n \sim (\beta_s^0)^{1/\phi_s} \qquad \text{(A.10)}$$

so our simple scaling argument implies the order of the adsorption phase transition should generally be $1/\phi_s$ within a simple scaling argument (see ref 6).

The preceding arguments are confined to the problem of adsorption on the outside of a surface. Qualitatively different behavior is known to occur for polymers adsorbed *into* semiconfined regions. For example, adsorption of random walks into a slitlike pore occurs as a first-order phase transition.[38] Helix–coil transitions, crudely related to the problem of adsorption onto a line, are known to sharpen in the presence of surfaces.[41] This general phenomenon may again be illustrated with a scaling argument. Consider for simplicity the situation of a polymer confined between two "parallel" hypersurfaces having the same surface interaction and separated by distance $\mathcal{L}$ in the $\mathbf{r}_\perp$ direction. If $\mathcal{L} \leq \langle \mathbf{R}^2 \rangle_f^{1/2}$, then the natural scaling distance of the polymer is no longer $\langle \mathbf{R}^2 \rangle_{0,f}$ but rather the separation $\mathcal{L}$. This is found explicitly by calculating the propagator $G^0(\mathbf{R}_\perp/\mathcal{L})$ for the confined geometry[13] which gives a new z_s^0 (confined) scaling variable upon scaling as in (A.8) to obtain

$$z_s^0(\text{confined}) = z_s^0(\text{unconfined})(\langle \mathbf{R}^2 \rangle_{0,f}/\mathcal{L}^2)^{d_\perp/2} \qquad \text{(A.11)}$$

Formally, if $\mathcal{L}$ becomes small and closer to the value of l than to $\langle \mathbf{R}^2 \rangle_{0,f}^{1/2}$, then ϕ_s approaches unity, and the transition becomes first order. Obviously this effect arises because the proximity of the confining surface increases the probability of intersection with the surface. This scaling argument *qualitatively* explains why confinement tends to sharpen the adsorption transition. This situation is contrasted with the more usual smoothing of transitions by finite boundaries in other areas of critical phenomena. In the near future we intend to calculate properties of polymers with excluded volume in confined regions using a generalization of the effective Hamiltonian formalism introduced by Nemirovsky and Freed.[22]

3. Moment $\langle |\mathbf{R}_\perp| \rangle$ for Penetrable and Impenetrable Surfaces. The odd moments $\langle \mathbf{R}_\perp^{2m+1} \rangle$ for a chain terminally attached to a penetrable surface vanish since there is an equal probability of the chain end being on either side of the surface. However, the moments $\langle |\mathbf{R}_\perp|^{2m+1} \rangle$ are generally nonzero where m is an integer. The moment $\langle |\mathbf{R}_\perp| \rangle$ is a particularly important example since it is frequently considered in Monte Carlo simulations of impenetrable surfaces.[4] A direct calculation through infinite order gives

$$\langle |\mathbf{R}_\perp| \rangle = \langle |\mathbf{R}_\perp| \rangle_0 \Gamma(3/2) \sum_{k=0}^{\infty} [-z_s^0 \Gamma(\epsilon_\perp/2)]^k / \Gamma[1 + (k\epsilon_\perp + 1)/2]/Q \qquad \text{(A.12)}$$

where the unperturbed value is

$$\langle |\mathbf{R}_\perp| \rangle_0 = (2\langle \mathbf{R}^2 \rangle_{0,f}/d)^{1/2} \Gamma[(d_\perp + 1)/2]/\Gamma(d_\perp/2) \qquad \text{(A.13)}$$

For $d_\perp = 1$ eq A.12 reduces to

$$\langle |\mathbf{R}_\perp| \rangle = \langle |\mathbf{R}_\perp| \rangle_0 \{\exp(\Delta_0^2) \times [\text{erf}(\Delta_0) - 1/\Delta_0^2]/\Delta_0 + 1/\Delta_0^3 + 1/\Delta_0\}/Q \qquad \text{(A.14)}$$

where $\Delta_0 = \Gamma(1/2) z_s^0$. Our $d_\perp = 1$ results for $\langle |\mathbf{R}_\perp| \rangle$ and $\langle |\mathbf{R}_\perp|^2 \rangle$ are found to be identical with those calculated previously be Nemirovsky and Freed[22] for Gaussian chains with an *impenetrable surface*, and generally we have

$$\langle |\mathbf{R}_\perp|^m \rangle_{\text{penetrable}} = \langle |\mathbf{R}_\perp|^m \rangle_{\text{impenetrable}} \qquad \text{(A.15)}$$

so that the distribution function for $|\mathbf{R}_\perp|$ is the *same* for both penetrable and impenetrable surfaces. Geometrically it is difficult to imagine the physical origin of this equivalence, but mathematically we are forced to accept it.

4. Ground-State-Dominant Propagator. The ground-state-dominant propagator is conveniently obtained from the moments $\langle |\mathbf{R}_\perp|^m \rangle$, which are

$$\langle |\mathbf{R}_\perp|^m \rangle = \langle |\mathbf{R}_\perp|^m \rangle_{z_s^0=0} (\Gamma(1 + m/2)/Q) \sum_{k=0}^{\infty} [-z_s^0 \Gamma(\epsilon_\perp/2)]^k / \Gamma(1 + m/2 + k\epsilon_\perp/2) \qquad \text{(A.16a)}$$

$$\langle |\mathbf{R}_\perp|^m \rangle_{z_s^0=0} = (2\langle \mathbf{R}^2 \rangle_{0,f}/d)^{m/2} \Gamma[(m + d_\perp)/2]/\Gamma(d_\perp/2) \qquad \text{(A.16b)}$$

For $z_s^0 \to -\infty$ this becomes asymptotically

$$\langle |\mathbf{R}_\perp|^m \rangle \sim \langle |\mathbf{R}_\perp|^m \rangle_{z_s^0=0} \Gamma(1 + m/2) |-z_s^0 \Gamma(\epsilon_\perp/2)|^{-m/\epsilon_\perp}; \quad z_s^0 \to -\infty \qquad \text{(A.16c)}$$

These moments correspond to the distribution function

$$G^\perp_{\text{gsd}}(z_s^0 \to -\infty) \propto (\hat{\mathbf{r}}_\perp)^{\epsilon_\perp/2} K_{\epsilon_\perp/2}(\hat{\mathbf{r}}_\perp) \qquad \text{(A.17a)}$$

where $K_{\epsilon_\perp/2}$ is a modified Bessel function of the third kind and where

$$\hat{\mathbf{r}}_\perp = (d/\xi_\perp^2)^{1/2} |\mathbf{R}_\perp|, \quad \xi_\perp^2 = |-z_s^0 \Gamma(\epsilon_\perp/2)|^{-2/\epsilon_\perp} (\langle \mathbf{R}^2 \rangle_{0,f}/2) \qquad \text{(A.17b)}$$

For large $\hat{\mathbf{r}}_\perp$ we have[16]

$$G^\perp_{\text{gsd}}(z_s^0 \to -\infty) \sim (\hat{\mathbf{r}}_\perp)^{(\epsilon_\perp - 1)/2} e^{-\hat{\mathbf{r}}_\perp} [1 + (\epsilon_\perp^2 - 1)/8\hat{\mathbf{r}}_\perp + \ldots] \qquad \text{(A.17c)}$$

so that $\xi_\perp$ has the interpretation of a correlation length. Using (A.7b) as an approximation the polymer–surface correlation length scales as

$$\xi_\perp \propto |T - \Theta_A|^{-\nu_\perp} \qquad \text{(A.17d)}$$

where the surface correlation exponent is $\nu_\perp = 1/\epsilon_\perp$. This form is very analogous to that found in the droplet model of Bruce and Wallace[42] for the droplet correlation length. The ground-state-dominant propagator (A.17) reduces to special cases considered previously[10-12] [see (4.12) for $\epsilon_\perp = 1$] and may be verified to be the solution of the differential equation

$$\frac{1}{2}\left[\frac{\partial^2}{\partial R_\perp^2} + \frac{d_\perp - 1}{R_\perp}\frac{\partial}{\partial R_\perp}\right] G^\perp_{\text{gsd}} = E_0(z_s^0) n_0 G^\perp_{\text{gsd}}, \qquad E_0 n_0 = |-z_s^0 \Gamma(\epsilon_\perp/2)|^{2/\epsilon_\perp} \qquad \text{(A.17e)}$$

where $G(R_\perp \to \infty) \to 0$. Equation A.17a is a starting point of a discussion of the leading effect of polymer–polymer excluded volume interaction for adsorbed chains. These calculations will be described in a subsequent paper.[17]

5. Other Partition Functions. Other important properties are the partition functions for loops, which return to the surface, for rings, and for star polymers attached to a surface. For example, a ring anchored to the

surface is characterized by $\mathbf{r} = 0$. Equation 3.4 then implies

$$Q_{\text{ring}} = Q_0(\text{ring})\hat{Q}$$
$$Q_0(\text{ring}) = Q(\text{ring};z_s^0 \to 0) = (d/2\pi\langle\mathbf{R}^2\rangle_{0,f})^{d/2} \quad \text{(A.18)}$$

where again through all orders we find

$$\hat{Q} = \sum_{k=0}^{\infty} \Gamma(\epsilon_\perp/2)[-z_s^0\Gamma(\epsilon_\perp/2)]^k/\Gamma[\epsilon_\perp(k+1)/2] \quad \text{(A.19)}$$

A loop which returns to the $d_\parallel$-dimension hypersurface has $\mathbf{r}_\perp = \mathbf{0}$, where $\mathbf{r}_\parallel$ is arbitrary. In this case a straightforward computation yields

$$Q(\text{loop}) = Q_0(\text{loop})\hat{Q}, \qquad Q_0(\text{loop}) = (d/2\pi\langle\mathbf{R}^2\rangle_{0,f})^{d_\perp/2} \quad \text{(A.20)}$$

The partition function for an f-arm star, having arms of equal length N_0 rooted at a common origin on the surface, is similarly calculated as

$$Q(f\text{-arm star}) = Q^f \quad \text{(A.21)}$$

because of the statistical independence of the arms when excluded volume is absent. Finally, we note that (A.19) reduces in $d_\perp = 1$ to

$$\hat{Q} = 1 - [\Gamma(1/2)z_s^0]^2 Q/z_s^0 \quad \text{(A.22)}$$

In closing this discussion of the partition functions we evaluate the exponents γ associated with the partition functions Q, Q(loop), Q(ring), Q(star), etc. The large-z_s^0 limit of (3.10) yields (see ref 2)

$$Q \sim n_0^{-\epsilon_\perp/2} \quad \text{(A.23)}$$

$$\gamma - 1 = -\epsilon_\perp/2, \qquad z_s^0 \to \infty, \qquad \epsilon_\perp > 0 \quad \text{(A.24)}$$

where $\gamma - 1$ is defined through the relation

$$Q \sim n_0^{\gamma-1} \quad \text{(A.25)}$$

Alternatively, the exponent γ can be obtained from the RG perturbation expansion. The RG theory defines this exponent by the fixed-point value of

$$\gamma - 1 = L_s \frac{\partial}{\partial L_s} \ln Z_Q \quad \text{(A.26)}$$

where Z_Q is the renormalization constant for the partition function Q which is introduced so that the renormalized partition function Q_R

$$Q_R \equiv Z_Q^{-1} Q \quad \text{(A.27)}$$

is well-defined for $\epsilon_\perp \to 0$ (i.e., all poles in $\epsilon_\perp$ are removed). Equations 3.6 and 4.4 enable Z_Q to be determined perturbatively as

$$Z_Q^{-1} = 1 + (2u_s/\epsilon_\perp) + (2u_s/\epsilon_\perp)^2 + \ldots \quad \text{(A.28)}$$

Substitution of (4.1) into (A.26) yields

$$\partial \ln Z_Q/\partial \ln L_s = -u_s + \mathcal{O}(\epsilon_\perp^3) \quad \text{(A.29)}$$

Since the fixed point u_s^* equals $\epsilon_\perp/2$ through second order in $\epsilon_\perp$, the RG prediction for γ is identical with the exact result for γ up to second order in $\epsilon_\perp$ (and presumably to higher order).

Applying the same RG procedure to determine γ(loop), γ(ring), and γ(f-arm star) for the polymer at an interacting surface yields

$$\gamma(\text{ring}) - 1 = -d/2 - 2u_s|_{u_s^*} + \mathcal{O}(\epsilon_\perp^3) \quad \text{(A.30a)}$$

$$\gamma(\text{loop}) - 1 = -d_\perp/2 - 2u_s|_{u_s^*} + \mathcal{O}(\epsilon_\perp^3) \quad \text{(A.30b)}$$

$$\gamma(f\text{-arm star}) - 1 = fu_s|_{u_s^*} + \mathcal{O}(\epsilon_\perp^2) \quad \text{(A.30c)}$$

It appears that the first order in $\epsilon_\perp$ RG theory for the polymer–surface interaction characteristically gives the *exact* value of these exponents. These expansions are to be contrasted with those for the polymer–polymer excluded volume in Appendix C.

Appendix B: Special Values of $\epsilon_\perp$

The solution to the polymer-adsorption problem is very useful for gaining further insight in the polymer–polymer excluded volume problem where there is no exact solution for comparison. A number of parallels between the theories are discussed in section IV. There are numerous other aspects of the polymer–polymer excluded volume problem for which the polymer–surface interaction problem is illuminating. First of all, we can investigate the surface interaction model *above* the critical dimension ($\epsilon_\perp < 0$). For example, for $\epsilon_\perp = -1$ the perturbation series in (3.6) is *divergent* but is still Borel summable,[8] and the partition function is easily shown to be [see (3.8)]

$$Q(\epsilon_\perp = -1) = \exp\{1/[z_s^0\Gamma(\epsilon_\perp/2)]^2\}\ \text{erfc}\ \{1/[\Gamma(\epsilon_\perp/2)z_s^0]\} \quad \text{(B.1)}$$

It is warned that from a physical standpoint the dimensional regularization scheme is potentially not meaningful for $\epsilon_\perp \le 0$ since cutoff terms neglected in (2.2c) begin to give an important contribution; this difficulty is ignored here. The usual log corrections at the critical dimension $\epsilon_\perp = 0$ are obtained by taking the limit $\epsilon_\perp \to 0$ in (4.9) where we recover the same leading corrections as obtained by Rubin[7] in his lattice model calculations.

The polymer–polymer Hamiltonian becomes ill-defined for $\beta_2^0 < 0$ unless a repulsive ternary interaction is introduced to stabilize the interaction.[18] A characteristic feature of the polymer model, when *formally* extended to negative interaction regime, is that the partition function becomes complex and nonanalytic.[42] This same type of behavior is found in the polymer interaction model if $\epsilon_\perp$ is *formally* taken as being large. For $\epsilon_\perp > 4$ we have from p 198 of Hardy[8]

$$Q \sim (2/\epsilon_\perp)\exp\{|z_s^0\Gamma(\epsilon_\perp/2)|^{2/\epsilon_\perp}\cos(2\pi/\epsilon_\perp)\} \times [\cos\{\sin(2\pi/\epsilon_\perp)|z_s^0\Gamma(\epsilon_\perp/2)|^{2/\epsilon_\perp}\} + i\sin\{\sin(2\pi/\epsilon_\perp)|z_s^0\Gamma(\epsilon_\perp/2)|^{2/\epsilon_\perp}\}], \qquad z_s^0 \to \infty \quad \text{(B.2)}$$

and

$$Q \sim (2/\epsilon_\perp)\exp\{|-z_s^0\Gamma(\epsilon_\perp/2)|^{2/\epsilon_\perp}\cos(2\pi/\epsilon_\perp)\} \times \cos\{\sin(2\pi/\epsilon_\perp)| - z_s^0\Gamma(\epsilon_\perp/2)|^{2/\epsilon_\perp}\}, \qquad z_s^0 \to -\infty \quad \text{(B.3)}$$

Equations B.2 and B.3 should serve as useful models in the study of nonperturbative renormalization where the systematics of the RG procedure are only partially understood.[42] For completeness the limits $\epsilon_\perp \to 4$ and $\epsilon_\perp \to 2$ lead to

$$Q = \cos(z_s^0)^{1/2}, \qquad z_s^0 \ge 0, \qquad \epsilon_\perp = 4 \quad \text{(B.4a)}$$

$$Q = \cosh(z_s^0)^{1/2}, \qquad z_s^0 \le 0, \qquad \epsilon_\perp = 4 \quad \text{(B.4b)}$$

$$Q = \exp(-z_s^0), \qquad \epsilon_\perp = 2 \quad \text{(B.5)}$$

Appendix C: Optimal Order of Truncation for the Polymer–Polymer Excluded Volume ϵ-Expansion

1. Illustrative Example. It is, in fact, possible to introduce particular properties of polymers with excluded volume where accurate solutions are available for comparison with ϵ expansions. As an example, consider the dimensions $\langle\mathbf{R}^2\rangle_{0_F}$ a swollen self-avoiding walk, cut the polymer in half to obtain $\langle\mathbf{R}^2\rangle_1$ and $\langle\mathbf{R}^2\rangle_2$ for the halves, and then compare the dimensions of the whole polymer

to the sum of its parts. The *exact* solution is

$$\langle \mathbf{R}^2 \rangle / (\langle \mathbf{R}^2 \rangle_1 + \langle \mathbf{R}^2 \rangle_2) = 2^{2\nu-1}, \qquad \langle \mathbf{R}^2 \rangle \sim n_0^{2\nu} \tag{C.1}$$

Using the best theoretical estimate of ν from Borel resummation,[43] ν(Borel) = 0.5885 ± 0.0025, implies the dimensionless ratio in (C.1) equals 1.131 ± 0.004. A first and second order in ϵ RG calculation gives for comparison

$$\langle \mathbf{R}^2 \rangle / (\langle \mathbf{R}^2 \rangle_1 + \langle \mathbf{R}^2 \rangle_2) = 1 + (\epsilon/8) \ln 2|_{d=3} + \mathcal{O}(\epsilon^2) = 1.09 \tag{C.2}$$

$$= 1 + (\epsilon/8) \ln 2 + [(15/4) \ln 2 + (\ln 2)^2](\epsilon/8)^2|_{d=3} + \mathcal{O}(\epsilon^3) = 1.13 \tag{C.3}$$

so that the first-order calculation has an error on the order of 4%, and the second-order calculation agrees with the Borel resummation result to within numerical uncertainty.

As opposed to the polymer–surface interaction problem, the addition of terms beyond second order in ϵ *does not* necessarily lead to an increasingly accurate expression for the ratio in (C.1). The ϵ expansion for the excluded volume interaction is thought to be asymptotic,[25,26] so that caution is needed in interpreting these ϵ expansions. There is a standard method for determining the "optimal order of truncation" of these series to obtain the best approximation, and we illustrate the method below for a few properties where the ϵ expansion is known through fourth order.[44]

2. Optimal Order of Truncation. Because the ϵ-perturbation expansion for the polymer–polymer interaction is presumably asymptotic, it should become less and less reliable beyond a certain order. Given high order in ϵ calculations, as well as knowledge of the limiting asymptotic values of the coefficients in the series, then Borel resummation techniques can be employed to resum the perturbation expansions. Frequently, however, such elaborate information is unavailable and, moreover, general techniques have not been devised to obtain full scaling functions using Borel resummation methods (see ref 45 however). There is a systematic and simple alternative to Borel resummation which guides the choice of the optimal order of truncation in the asymptotic perturbation expansion. We now employ this method and compare the results with those of the Borel resummation in the limited number of cases where this is possible. From this analysis we infer that, as a rule of thumb, the second order in ϵ theory is the optimal order of truncation.

Substantial effort has already been made to calculate the ϵ expansions for various properties. For example, Tarasov et al.[44] calculate 2ν, the exponent γ, and the dimensionless coupling constant u_2^*, respectively, as

$$2\nu - 1 = \epsilon/8 + (15/4)(\epsilon/8)^2 + [135/8 - 33\hat{\zeta}(3)](\epsilon/8)^3 + [3799/64 - 873\hat{\zeta}(3)/4 - 198\hat{\zeta}(4) + 930\hat{\zeta}(5)](\epsilon/8)^4 + \mathcal{O}(\epsilon^5) \tag{C.4}$$

$$\gamma - 1 = \epsilon/8 + (13/4)(\epsilon/8)^2 + [93/8 - 33\hat{\zeta}(3)](\epsilon/8)^3 + [1965/64 - 741\hat{\zeta}(3)/4 - 198\hat{\zeta}(4) + 930\hat{\zeta}(5)](\epsilon/8)^4 + \mathcal{O}(\epsilon^5) \tag{C.5}$$

$$u_2^* = \epsilon/8 + (21/4)(\epsilon/8)^2 + [71/8 - 33\hat{\zeta}(3)](\epsilon/8)^3 + [4139/192 - 1133\hat{\zeta}(3)/4 - 132\hat{\zeta}(4) + 930\hat{\zeta}(5)](\epsilon/8)^4 + \mathcal{O}(\epsilon^5) \tag{C.6}$$

where $\hat{\zeta}$ denotes the Riemann zeta function. A similar pattern appears in the magnitude of the coefficients. Asymptotically all these series have coefficients[21,42] of order ϵ^k of

$$a_k \sim k!(-3/8)^k k^b(\text{constant}) \tag{C.7}$$

implying a zero radius of convergence[21] for the series. The constant b equals 4 for u_2^*, and it generally depends on the property considered.[21]

It is frequently argued that, because of the zero radius of convergence, *no reliable conclusions*[44] can be obtained by setting $\epsilon = 1$ in these series. This is not true, and rather good and justifiable results can be obtained by using the optimal truncation. This optimal truncation[31] is obtained for a given value of ϵ by first evaluating successive terms in the ϵ expansion and by then identifying the minimum magnitude term before the expansion coefficients start growing rapidly. Fortunately, such a minimum term frequently arises at relatively low order in perturbation theory, and in $d = 3$, for example, we have for ν, γ, and u_2^*, respectively

$$2\nu - 1 = 0.125 + 0.059 - 0.045 + 0.134 \tag{C.8}$$

$$\gamma - 1 = 0.125 + 0.051 - 0.055 + 0.136 \tag{C.9}$$

$$u_2^* = 0.125 + 0.082 - 0.060 + 0.131 \tag{C.10}$$

The optimal order of truncation involves truncating the smallest magnitude term *and* all higher order terms so that in $d = 3$ we obtain

$$\nu(\text{optimal truncation}) = 0.592 \pm 0.045 \tag{C.11}$$

$$u_2^*(\text{optimal truncation}) = 0.207 \pm 0.060 \tag{C.12}$$

where a bound on the magnitude of the error is estimated as the first neglected term in the series. Interestingly, the exponent γ is a borderline case, and strictly the *first order in* ϵ theory is the optimal order of truncation. In such a borderline case it is, however, reasonable to take an average of the second-order and first-order expressions ($d = 3$), yielding

$$\gamma(\text{optimal; } d = 3) = 1.125 \tag{C.13a}$$

$$\bar{\gamma} = [\gamma(\text{first order}) + \gamma(\text{second order})]/2 = 1.15 \tag{C.13b}$$

For comparison, the most recent Borel resummation values are[43]

$$\nu(\text{Borel}) = 0.5885 \pm 0.0025 \tag{C.14}$$

$$\gamma(\text{Borel}) = 1.160 \pm 0.004 \tag{C.15}$$

based upon fifth order in ϵ perturbation theory where the errors are estimates of precision rather than accuracy since a number of assumptions are implicit in (C.14) and (C.15). These "best estimates" from Borel resummation are in quite respectable agreement with the optimal truncation predictions. The main advantages of optimal truncation, beyond its relative simplicity, is that it enables the accurate approximation of *crossover* scaling functions, when applied to series such as (4.18), and moreover the method is systematic.

At present optimal truncation appears to be the only practical option for determining the full crossover functions. There is, however, intensive work to extend the Borel resummation method to describe crossover[45] for the property $\langle \mathbf{R}^2 \rangle_f$. It is anticipated, however, that the high-order perturbative calculations, which the Borel resummation requires as its input, will not be available for some time for the many properties of interest. It is also not yet clear how to treat the case of multiple interactions within the Borel resummation scheme.

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$$f(z) = \sum_{k=0}^{\infty} a_k z^k$$

where the a_k may diverge factorially. The generalized Borel transform $B_{\mu,\epsilon_\perp/2}$ of the series is defined as

$$B_{\mu,\epsilon_\perp/2}(z) = \sum_{k=0}^{\infty} a_k z^k / \Gamma(k\epsilon_\perp/2 + \mu + 1)$$

[see (3.6) and (3.7e)]. The Borel sum of $f(z)$ formally equals

$$f(z) = \int_0^\infty e^{-t} t^\mu B_{\mu,\epsilon_\perp/2}(z t^{\epsilon_\perp/2})\, dt$$

Frequently the special limit $\epsilon_\perp \to 0$ (ordinary Borel resummation) is considered since the transform is simple to manipulate.[8] See also ref 8 and 21.
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Mutual Diffusion in Concentrated Polymer Solutions under a Small Driving Force

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ABSTRACT: A theory is presented for mutual diffusion in concentrated polymer solutions under a small driving force. The crucial concept is that the interdiffusion of polymer and solvent causes deformation of the polymer component. A memory integral contribution to the solvent flux is developed from the transient network and reptation models; analytical formulas for measurables are derived for a polymer behaving like a Maxwell fluid. For sorption experiments, non-Fickian behavior is predicted when the polymer relaxation time matches the sorption time scale, that is, when the diffusion Deborah number is $\sim\mathcal{O}(1)$. The predictions agree with non-Fickian behavior observed in classical and oscillatory sorption experiments. The analysis clarifies the potential value of the oscillatory sorption technique.

I. Introduction

The diffusion of a low molecular weight species in high polymer systems over a macroscopic length scale is often the rate-controlling process in industrial processing operations; examples include fiber spinning, film casting, and coatings processes. The effective design of these requires a quantitative description of the diffusion. Our recent work[1,2] focuses on mutual diffusion in concentrated polymer solutions under a small driving force, that is, the interdiffusion of solvent and polymer in the presence of a slight composition gradient. A theory based on the physical arguments of Thomas and Windle[3] compares reasonably well with data over a range of conditions encompassing the so-called viscoelastic[4,5] or non-Fickian regime. In this article we present an alternate development of the theory and analyze sorption under a small driving force.

II. Sorption Experiments

In the classical sorption experiment, a polymer solution is held in contact with a large reservoir of solvent vapor at temperature T and pressure P. The solvent activity in the vapor, $a(t)$, is increased in a step

$$a(t) = a^- + AH(t) \qquad \text{(II.1)}$$

causing diffusion of solvent into the solution. Here, a^- is the activity before the step ($0 < a^- < 1$), $H(t)$ is the step function, and A is the amplitude of the step ($a^- + A < 1$). Commonly, one observes the total mass of solvent in the solution, $M(t)$. In a more general experiment

$$a(t) = a^- + Ag(t) \qquad \text{(II.2)}$$

where $g(t)$ is a bounded, piecewise continuous function. (If $-1 < g(t) < 1$, then A lies in a range such that $0 < a^- - A$ and $a^- + A < 1$.)

Very little experimental work has been done with $g(t) \neq H(t)$. Vrentas, Duda, and co-workers[6] reported recently on a technique using $g(t) = \sin \omega t$. The method, called oscillatory sorption, appears promising for the study of mutual diffusion in polymer solutions and is analyzed subsequently in some detail.

For simplicity we consider sorption in one-dimensional systems (Figure 1) having an average depth l and allow only small fluctuations in $a(t)$; i.e., $A \ll 1$. Before we continue, a summary of previous work is given.

III. Previous Theory

Mutual diffusion on a macroscopic length scale (say >10 μm) is described adequately by the species continuity equations together with constitutive relationships for the

0024-9297/86/2219-2220$01.50/0